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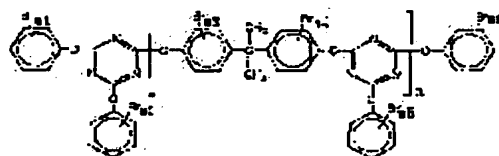
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## (54) CROSSLINKABLE NORBORNENE RESIN COMPOSITION AND MOLDING MADE THEREFROM

(57)Abstract:

PURPOSE: To obtain the subject composition which can give a molding improved in electrical insulation properties, heat resistance, chemical resistance, etc., by mixing a thermoplastic hydrogenated ring-opening norbornene resin with an organic peroxide, a crosslinking aid and a specified flame retardant.

CONSTITUTION: 100 pts.wt. thermoplastic hydrogenated ring-opening norbornene resin of a molecular weight of 10000-200000 and a degree of hydrogenation of 90% or above is melt-mixed with 0.001-30 pts.wt. organic peroxide, 0.1-10 pts.wt. wt., per pt.wt. organic peroxide, crosslinking aid and optionally 5-150 pts.wt. flame retardant of formula I or II (wherein (n) and m1 to M6 integers;  $n \geq 0$ ;  $1 \leq m1 \leq 5$ ;  $1 \leq m2 \leq 5$ ;  $1 \leq m3 \leq 4$ ;  $1 \leq m4 \leq 5$ ;  $1 \leq m5 \leq 5$ ; and  $1 \leq m6 \leq 5$ ) to obtain a resin composition. This resin composition is molded and crosslinked at 80-350° C for 5-120 min to obtain a crosslinked molding having a water absorptivity of 0.03% or below, an insulation resistance of 10<sup>15</sup> to 10<sup>17</sup>Ω, a dielectric constant of 2.0-2.5 at 1MHz and a dielectric loss tangent of 0.0001-0.0007.



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**CROSS-LINKABLE NORBORNENE RESIN COMPOSITION  
AND MOLDED ARTICLE COMPOSED THEREOF**

## BACKGROUND OF THE INVENTION

### FIELD OF THE INVENTION

This invention relates to a cross-linkable norbornene resin composition excellent in electrical  
5 insulation properties, a cross-linkable molded article composed thereof, and a cross-linked molded article.

### RELATED ART

In the field of precision equipment such as electronic computer, communication equipment or the like,  
10 demands of high speed operation, high reliability, high density and the like increase accompanying the progress of technique, and now, making circuit board have higher performance such as multilayering, making precision higher, micronization or the like, is proceeding.

15 Heretofore, phenol resin, epoxy resin, polyimide resin, fluoroplastics, polybutadiene resin and the like have been used for such circuit board substrate, and are being improved in response to progress of technique (see Japanese Patent Application Kokai No.  
20 60-84,317; Japanese Patent Application Kokai No. 60-258,233; Japanese Patent Application Kokai No. 3-37,256; Japanese Patent Application Kokai No. 3-55,327; Japanese Patent Application Kokai No. 3-166,256; Japanese Patent Application Kokai No. 3-275,760 and the like).

25 However, thermosetting resins such as phenol

resin, epoxy resin, polyimide resin and the like have a high dielectric constant of 4.0 or more and a high loss tangent of 0.01 or more, and hence, the electric characteristics thereof are unsatisfactory. When these resin are used in circuit board substrates, it is difficult to conduct the operation at a high speed with high reliability. On the other hand, when a thermoplastic resin such as fluoroplastic, polybutadiene resin or the like is used, a laminate of prepreg formed therefrom is inferior in heat resistance, and hence, causes sometimes cracks and peeling in soldering and the like and is inferior in dimension stability. Hence, multilayering is difficult.

Recently, a method has been proposed for improving the heat resistance, solvent resistance and the like of a thermoplastic norbornene resin by subjecting the same to organic peroxide cross-linking. For example, Japanese Patent Application Kokai No. 62-34,924 discloses a method comprising kneading a resin with a cross-linking agent, then grinding the mixture, impregnating the same with an organic peroxide solution, removing the solvent and then press-molding the same to cross-link the resin. However, such a procedure requires complex steps, and its efficiency is low, so that the organic peroxide is not always dispersed uniformly. The thermoplastic norbornene resin disclosed in said Japanese publication is a copolymer of a norbornene monomer and ethylene, and when it is intended to cross-link in said manner a hydrogenated

ring-opened norbornene resin which is not disclosed therein, the molecular weight is often reduced owing to degradation of the polymer, and the heat resistance necessary for soldering cannot be obtained.

5                    Japanese Patent Application Kokai No. 2-255,848 discloses cross-linking a resin composition of a thermoplastic norbornene resin including a hydrogenated ring-opened norbornene resin and a non-crystalline or low-crystalline  $\alpha$ -olefin copolymer and a non-crystalline or  
10 low-crystalline styrene copolymer with an organic peroxide. However, it has no specific example of cross-linking the hydrogenated ring-opened norbornene resin, and does not disclose cross-linking a hydrogenated ring-opened norbornene resin which is not blended with said  
15 special resin. Furthermore, said Japanese publication discloses a method of cross-linking a compound of such a resin composition with an organic peroxide, a cross-linking coagent and a flame retarder and a method of cross-linking a mixture of the resin with an organic  
20 peroxide and then compounding the cross-linked resin with a retarder. However, in the method of compounding a flame retarder after the cross-linking, the flame retarder is difficult to disperse uniformly in the cross-linked resin when used in a laminate of prepreg or the  
25 like, and hence, said method is not practical. Also, in the case of compounding the flame retarder before the cross-linking, the flame retarder mentioned in said publication deteriorates the organic peroxide to make it

impossible to obtain a sufficient retardance.

#### SUMMARY OF THE INVENTION

The present inventors have made extensive research aiming at development of a molded article  
5 consisting of a resin excellent in heat resistance and having a low dielectric constant and a low loss tangent, to find that when an organic peroxide and a cross-linking coagent are uniformly dispersed in a thermoplastic, hydrogenated, ring-opened norbornene resin, the polymer  
10 can be cross-linked without causing decomposition of the polymer.

According to this invention, there is provided a uniform, cross-linkable norbornene resin composition comprising 100 parts by weight of a thermoplastic,  
15 hydrogenated, ring-opened norbornene resin having dispersed therein 0.001 to 30 parts by weight of an organic peroxide and 0.1 to 10 parts by weight, per part by weight of the organic peroxide, of a cross-linking coagent, and also a cross-linkable molded article  
20 consisting of the cross-linkable resin composition, as well as a cross-linked molded article of the resin composition.

#### DETAILED DESCRIPTION OF THE INVENTION

##### Thermoplastic, hydrogenated, ring-opened norbornene resin

25 The thermoplastic, hydrogenated, ring-opened norbornene resin used in this invention is a resin known

in Japanese Patent Application Kokai No. 3-14,882,  
Japanese Patent Application Kokai No. 3-122,137 and the  
like. Specifically, it is a hydrogenation product of a  
polymer obtained by ring-opening polymerization of a  
5 norbornene monomer.

Norbornene monomers are known in the above-  
mentioned Japanese publications, Japanese Patent Applica-  
tion Kokai No. 2-227,424, Japanese Patent Application  
Kokai No. 2-276,842 and the like, and include, for  
10 example, norbornene; alkyl-, alkylation- and aromatic-  
substituted products of norbornene; polar group (e.g.  
halogen, hydroxy, ester, ulcus, cyano, amido, imido and  
the like)-substituted derivatives of the above  
unsubstituted and substituted norbornenes, for example,  
15 2-norbornene, 5-methyl-2-norbornene, 5,5-dimethyl-2-  
norbornene, 5-ethyl-2-norbornene, 5-butyl-2-norbornene,  
5-ethylidene-2-norbornene, 5-methoxycarbonyl-2-  
norbornene, 5-cyano-2-norbornene, 5-methyl-5-methoxy-  
carbonyl-2-norbornene, 5-phenyl-2-norbornene, 5-phenyl-5-  
20 methyl-2-norbornene and the like; cyclopentadiene  
oligomers formed as a result of radical addition, their  
derivatives and substituted products similar to those  
mentioned above as to norbornene, for example, cyclo-  
pentadiene, 2,3-dihydrodicyclopentadiene, 1,4:5,8-  
25 dimethano-1,2,3,4,4a,5,8,8a-2,3-cyclopentadieno-  
naphthalene, 6-ethyl-1,4:5,8-dimethano-  
1,4,4a,5,6,7,8,8a-octahydronaphthalene, 1,4:5,10:6,9-tri-  
methano-1,2,3,4,4a,5,5a,6,9,9a,10,10a-dodecahydro-2,3-



cyclopentadienoanthracene and the like; adducts of cyclopentadiene and tetrahydroindene or the like and their derivatives and substituted products similar to those mentioned above as to norbornene, for example, 1,4-methano-1,4,4a,4b,5,8,8a,9a-octahydrofluorene, 5,8-methano-1,2,3,4,4a,5,8,8a-octahydro-2,3-cyclopentadienonaphthalene and the like; etc.

Ring-opening polymerization of norbornene monomers may be conducted in a known manner, and if necessary, the norbornene monomers may be copolymerized with other copolymerizable monomers. The polymer may be modified with an  $\alpha,\beta$ -unsaturated carboxylic acid and/or its derivative, a styrenic hydrocarbon, an organosilicon compound having an olefinically unsaturated bond and a hydrolyzable group or an unsaturated epoxy monomer. These resins are hydrogenated into thermoplastic, hydrogenated, ring-opened norbornene resins. After the hydrogenation, the hydrogenated resins may be modified.

The molecular weight is suitably 10,000 to 200,000 in terms of number average molecular weight as measured by GPC (gel permeation chromatography) analysis using cyclohexane as a solvent. When hydrogenation is conducted, the hydrogenation degree is 90% or more, preferably 95% or more, and more preferably 99% or more in order to enhance the photo-deterioration resistance and weather deterioration resistance.

The thermoplastic, hydrogenated, ring-opened norbornene resin of this invention may have added

thereto, if necessary, various additives such as anti-oxidant of phenol type, phosphorus type or the like; heat deterioration inhibitor of phenol type or the like; ultraviolet light stabilizer of benzophenone type or the like; antistatic agent of amine type or the like; lubricant such as ester of aliphatic alcohol, partial ester of polyhydric alcohol or the like; etc.

#### Organic peroxide

The organic peroxide used in this invention is not critical, and may be those known in Japanese Patent Application Kokai No. 62-34,924 and the like, including, for example, hydroperoxides such as t-butyl hydroperoxide, cumene hydroperoxide and the like; dialkyl peroxides such as dicumyl peroxide, t-butylcumyl peroxide,  $\alpha,\alpha'$ -bis(t-butylperoxy-m-isopropyl)benzene and the like; diacyl peroxides such as dipropionyl peroxide, benzoyl peroxide and the like; peroxy ketals such as 2,5-dimethyl-2,5-di(t-butylperoxy)hexane, 2,5-dimethyl-2,5-di(t-butylperoxy)hexyne-3, 1,3-di(t-butylperoxyisopropyl)benzene and the like; peroxyesters such as t-butyl peroxyacetate, t-butyl peroxybenzoate and the like; peroxycarbonates such as t-butylperoxyisopropyl carbonate, di(isopropylperoxy) dicarbonate and the like; ketone peroxides such as methyl ethyl ketone peroxide, methyl isobutyl ketone peroxide and the like; etc.

#### Cross-linking coagent

The cross-linking coagent used in this invention is not critical, and may be those known in Japanese

Patent Application Kokai No. 62-34,924 and the like, including, for example, oxime or nitroso type cross-linking coagents such as quinone dioxime, benzoquinone dioxime, p-nitrosophenol and the like; maleimide type  
5 cross-linking coagents such as N,N-m-phenylene bismaleimide and the like; allyl type cross-linking coagents such as diallyl phthalate, triallyl cyanurate, triallyl isocyanurate and the like; methacrylate type cross-linking coagents such as ethylene glycol  
10 dimethacrylate, trimethylolpropane trimethacrylate and the like; vinyl type cross-linking coagents such as vinyltoluene, ethylvinylbenzene, divinylbenzene and the like; etc. Among them, allyl type cross-linking coagents and methacrylate type cross-linking coagents are easy to  
15 disperse uniformly and hence preferred.

Cross-linkable norbornene resin composition

The cross-linkable norbornene resin composition of this invention is a uniform composition consisting of a thermoplastic, hydrogenated, ring-opened norbornene  
20 resin having added thereto an organic peroxide and a cross-linking coagent.

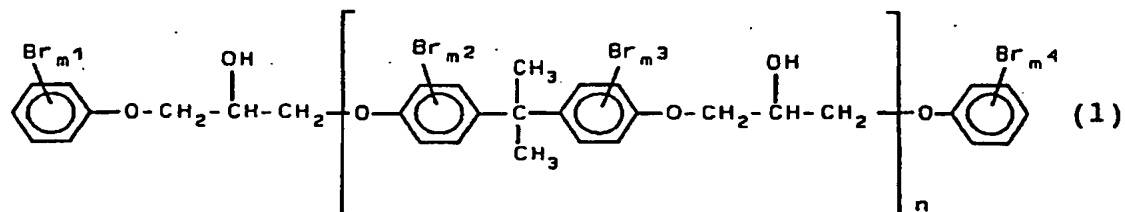
When the amount of the organic peroxide added is too small, cross-linking becomes difficult to cause, and therefore, the organic peroxide is added in an amount  
25 of 0.001 part by weight or more, preferably 0.01 part by weight or more, and more preferably 0.05 part by weight or more, most preferably 0.1 part by weight or more per 100 parts by weight of the thermoplastic, hydrogenated,

ring-opened norbornene resin. When the amount of the organic peroxide added is too large, the electric characteristics, water resistance, moisture resistance and the like of the cross-linked resin are deteriorated, and hence, the organic peroxide is added so as not to exceed 30 parts by weight, preferably 15 parts by weight, more preferably 10 parts by weight, and most preferably 5 parts by weight, per 100 parts by weight of the thermoplastic, hydrogenated, ring-opened norbornene resin.

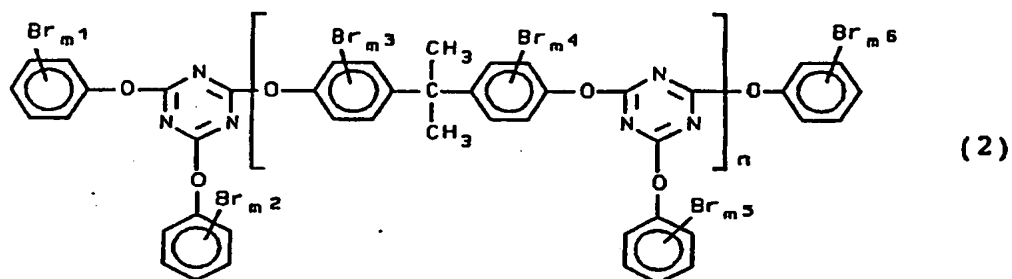
10           The amount of the cross-linking coagent added is 0.1 to 10 parts by weight, preferably 0.2 to 5 parts by weight, per part by weight of the organic peroxide. When the amount of the cross-linking coagent added is too small, cross-linking is difficult to cause, and the thermoplastic, ring-opened norbornene resin tends to be decomposed to a lower molecular weight resin, and hence, the heat resistance necessary for soldering cannot be obtained. When the amount of the cross-linking coagent is too large, the electric characteristics, water resistance and moisture resistance of the cross-linked resin are deteriorated, and hence, such an amount is not desirable.

25           In order to enhance the flame retardance of the cross-linked molded article of this invention, it is preferable to uniformly disperse a flame retarder in the norbornene resin composition of this invention. The flame retarder used in this invention is those capable of being uniformly dispersed in the resin composition, and

preferably those which are not modified or deteriorated by an organic peroxide in the resin composition or in the process of cross-linking reaction. Specific examples of the flame retarder include flame retarders represented by  
5 formula (1):



wherein  $n$ ,  $m^1$ ,  $m^2$ ,  $m^3$  and  $m^4$  are integers and satisfy  $n \geq 0$ ,  $1 \leq m^1 \leq 5$ ,  $1 \leq m^2 \leq 4$ ,  $1 \leq m^3 \leq 4$ , and  $1 \leq m^4 \leq 5$ , preferably  $2 \leq m^1 \leq 4$ ,  $2 \leq m^2 \leq 3$ ,  $2 \leq m^3 \leq 3$ , and  $2 \leq m^4 \leq 4$ , and more preferably  $m^1 = 3$ ,  $m^2 = 2$ ,  $m^3 = 2$ , and  $m^4 = 3$ ,  
10 and formula (2):



wherein  $n$ ,  $m^1$ ,  $m^2$ ,  $m^3$ ,  $m^4$ ,  $m^5$ , and  $m^6$  are integers and satisfy  $n \geq 0$ ,  $1 \leq m^1 \leq 5$ ,  $1 \leq m^2 \leq 5$ ,  $1 \leq m^3 \leq 4$ ,  $1 \leq m^4 \leq 4$ ,  $1 \leq m^5 \leq 5$ , and  $1 \leq m^6 \leq 5$ , preferably  $2 \leq m^1 \leq 4$ ,  $2 \leq m^2 \leq 4$ ,  $2 \leq m^3 \leq 3$ ,  $2 \leq m^4 \leq 3$ ,  $2 \leq m^5 \leq 4$ , and  $2 \leq m^6 \leq 4$ , and particularly preferably  $m^1 = 3$ ,  $m^2 = 3$ ,  $m^3 = 2$ ,  $m^4 = 2$ ,  $m^5 = 3$  and  $m^6 = 3$ , and these flame retarders can be uni-  
15 formly dispersed and are not modified nor deteriorated by

the organic peroxide.. The amount of the flame retarder added is 5 to 150 parts by weight, preferably 20 to 140 parts by weight, more preferably 40 to 120 parts by weight, per 100 parts by weight of the thermoplastic, hydrogenated, ring-opened norbornene resin.

The method of uniformly dispersing an organic peroxide and a cross-linking coagent in a thermoplastic, hydrogenated, ring-opened norbornene resin includes a method in which mixing and dispersing are effected in a solution of the thermoplastic, hydrogenated, ring-opened norbornene resin and then the solvent is removed and a method in which mixing and dispersing are effected in the molten state of the thermoplastic, hydrogenated, ring-opened norbornene resin. The solvent of the thermoplastic, hydrogenated, ring-opened norbornene resin solution may be any solvent as far as it dissolves the thermoplastic, hydrogenated, ring-opened norbornene resin and is not critical. For example, toluene, xylene, ethylbenzene, chlorobenzene and the like may be used. Incidentally, in the method in which the thermoplastic, hydrogenated, ring-opened norbornene resin is melted and the organic peroxide and the like are added, the melting, mixing and dispersing have to be possible at a temperature at which the resin is not cross-linked, and therefore, this method cannot be applied to some combinations of thermoplastic, hydrogenated, ring-opened norbornene resin, organic peroxide and cross-linking coagent. Even in the method in which the organic peroxide and cross-

linking coagent are added to the thermoplastic, hydrogenated, ring-opened norbornene resin solution, the heating to remove the solvent must be effected at such a temperature that no cross-linking is caused.

5 Cross-linkable molded article

In this invention, the cross-linkable norbornene resin composition is molded and then cross-linked to obtain a cross-linkable molded article.

In the molding of the cross-linkable norbornene  
10 resin composition, a solution in a solvent of the cross-linkable norbornene resin composition is subjected to molding so as to prevent the moldability from being deteriorated owing to cross-linking during the molding, or the cross-linkable norbornene resin composition is  
15 melted and molded at a temperature at which the thermoplastic, hydrogenated, ring-opened norbornene resin is not cross-linked or cross-linking thereof is sufficiently slow. As the solvent, the above-mentioned solvents in which the thermoplastic, hydrogenated, ring-opened  
20 norbornene resin is dissolved are used. In general, the cross-linkable norbornene resin composition is dissolved in a solvent and then molded.

Specifically, the cross-linkable norbornene resin composition dissolved in a solvent is casted to  
25 form a sheet or film, or alternatively, a cloth-like substrate such as glass cloth, aramid cloth, polyester cloth, nylon cloth or the like or a mat-form substrate of the same material as the cloth-like substrate is

impregnated with the cross-linkable norbornene resin composition, and then the impregnated substrate is molded. The cross-linkable molded article of the substrate impregnated with the cross-linkable norbornene resin composition includes a prepreg.

#### Cross-linking

In this invention, a cross-linked molded article is obtained by heating the cross-linkable molded article to a temperature higher than the definite temperature to cause cross-linking. The temperature at which the cross-linking is caused is determined depending mainly upon a combination of the organic peroxide and the cross-linking coagent; however, the cross-linking is conducted at a temperature of preferably 80 to 350°C, more preferably 120 to 300°C and most preferably 150 to 250°C. The cross-linking time is preferably about four times the half-life period of the organic peroxide. Specifically, it is preferably 5 to 120 minutes, more preferably 10 to 90 minutes, and most preferably 20 to 60 minutes.

#### Cross-linked molded article

The cross-linked molded article of this invention includes a laminate, an interlaminar insulating film, a moistureproof layer-forming film and the like in the cross-linked state.

The cross-linked molded article of this invention has usually a water absorption of 0.03% or less, an insulation resistance of  $10^{15}$  to  $10^{17}\Omega$ , a dielectric



constant at 1 MHz of 2.0 to 2.5 and a loss tangent at 1  
MHz of 0.0001 to 0.0007, and is superior to conventional  
thermosetting resin molded articles in respects of water  
resistance and electric characteristics. On the other  
5 hand, the heat resistance is equivalent to that of the  
conventional thermosetting resin molded articles, and  
even when a solder at 260°C is contacted with a laminate  
of a copper foil to the cross-linked molded article of  
this invention for 30 seconds, no abnormal phenomena such  
10 as peeling of copper foil, blistering and the like are  
observed. From these facts, the laminate which is the  
cross-linked molded article of this invention is suitable  
as a circuit board substrate.

The cross-linked molded article of this inven-  
15 tion is also excellent in flame retardance, and specifi-  
cally in the UL-94 specification, it is preferable for  
the molded article to exhibit a flame retardance value of  
V-2 or better, more preferable to exhibit V-1 or V-0, and  
most preferable to exhibit V-0. In order to obtain such  
20 cross-linked molded articles, it is sufficient to use the  
above-mentioned flame retarder-containing, cross-link-  
able, norbornene resin composition.

#### Prepreg

In a prepreg which is one of the embodiments of  
25 the cross-linkable molded article of this invention, its  
substrate is not critical, and may be a cloth-like  
substrate such as glass cloth, aramid cloth, polyester  
cloth, nylon cloth or the like; a mat-form substrate of

the same material as that of the cloth-like substrate; a nonwoven fabric; a craft paper; a linter paper; or the like.

The production of a prepreg using the cross-  
5 linkable norbornene resin composition of this invention may be carried out in a known manner, for example, by dissolving the cross-linkable norbornene resin composition in a solvent such as toluene, cyclohexane, xylene or the like at a concentration of about 5 to 50% by weight,  
10 immersing the substrate in the resulting solution, and then drying the substrate to remove the solvent. In general, the prepreg is preferably formed so as to have a thickness of about 50 to 500  $\mu\text{m}$ .

#### Sheet

15 The method of producing a sheet which is one of the embodiments of the cross-linkable molded article of this invention is not critical. In general, a casting method is used. For example, a sheet is prepared by dissolving and dispersing the cross-linkable norbornene  
20 resin composition of this invention in a solvent such as toluene, xylene, cyclohexane or the like so that the concentration may become about 5 to 50% by weight, casting or coating the resulting solution on a smooth surface, removing the solvent by drying or the like and  
25 peeling the resulting film from the smooth surface. In the case of removing the solvent by drying, it is preferable to select such a method that foaming is not caused owing to rapid drying, for example, it is

preferred to volatilize the solvent to some extent at a low temperature and then elevate the temperature to sufficiently volatilize the solvent. As the smooth surface, a planished metal plate, a carrier film of resin or the like may be used. In the case of use of the carrier film of resin, care should be paid to the solvent resistance and heat resistance of the material of the carrier film in determining the solvent and drying conditions to be used. The sheet obtained by the casting method has generally a thickness of about 10  $\mu$ m to 1 mm. This sheet can be cross-linked and then used as an interlaminar insulating film, a moistureproof layer-forming film or the like.

#### Laminate

The laminate which is one of the embodiments of the cross-linked molded article of this invention is prepared by putting a plurality of sheets of the above-mentioned prepreg and/or uncross-linked sheet one on another so that the desired thickness of laminate may be obtained and hot press-molding the resulting assembly to cross-link and fuse the same. When the laminate is used as a circuit board substrate, a circuit is formed by laminating a conductive layer for wiring to the laminate and etching the surface. The conductive layer for wiring is not necessarily laminated to the outer surface of the laminate which is the finished product, and for some purposes, it may be laminated to the interior of the laminate. In order to prevent the laminate from being

warped during the fabrication such as etching or the like, it is preferable to laminate the upper layer and the lower layer symmetrically. The heat press-molding method is not critical, and may be a conventional method.

- 5 For example, the surface of the prepreg and/or assembly is heated to a temperature not lower than the fusing temperature of the cross-linkable norbornene resin composition used, usually about 150 to 300°C, pressed at about 30 to 80 kgf/cm<sup>2</sup>, to cross-link and fuse the layers  
10 to one another to obtain a laminate.

#### DESCRIPTION OF REFERRED EMBODIMENTS

This invention is further explained in detail referring to Examples and Comparative Examples.

- Incidentally, the insulation resistance, dielectric  
15 constant, loss tangent and water absorption were measured according to JIS C 648.

The flame retardance was evaluated by the following method in accordance with the UL-94 specification:

- 20 Using a test specimen having a thickness of 1/16 inch, the upper end of the test specimen was clamped to fix the same vertically and cotton was spreaded at the place 12 inches under the test specimen. A flame of a gas burner was applied to the lower end of the test  
25 specimen for ten seconds and the first burning time of the test specimen was measured. When the fire went out, a flame of a gas burner was again applied to the lower

end of the test specimen for ten seconds and the second burning time of the test specimen was measured. Ten data in total were obtained about the first and second burning times of five test specimens, the total thereof was taken  
5 as T, the maximum data was taken as M, and the test specimens were judged as V-0, V-1, V-2 and failure based on the following criterion:

V-0: T was 50 seconds or less and M is 10 seconds or less, the specimen did not burn up to the  
10 clamp, and there was no case where a molten piece with flame fell down to ignite the cotton.

V-1: T was 250 seconds or less, M was 30 seconds or less, the test specimen did not burn up to the clamp and there was no case where a molten piece with  
15 flame fell down to ignite the cotton.

V-2: T was 250 seconds or less, M was 30 seconds or less and a molten piece with flame fell down to ignite the cotton.

Failure: Did not satisfy the requirements for  
20 V-1, V-2 and V-3.

#### Example 1

In 80 parts by weight of toluene were dispersed 20 parts by weight of a thermoplastic, hydrogenated, ring-opened norbornene resin (ZEONEX 280, a trade name of  
25 Nippon Zeon Co., Ltd., glass transition temperature: 140°C, number average molecular weight: about 28,000, hydrogenated degree: more than 99.7%), 1 part by weight

of  $\alpha, \alpha'$ -bis(t-butylperoxy-m-isopropyl)benzene and 1 part by weight of diallyl phthalate to obtain a uniform solution without causing precipitation and the like.

#### Example 2

5           The cross-linkable norbornene resin composition solution obtained in Example 1 was coated on a planished SUS plate by a coating machine so that the thickness of the coating film might become 750  $\mu\text{m}$ , and allowed to stand at 60°C for 20 minutes and then at 120°C for 10  
10 minutes to dry the coating film. The coating film was peeled from the SUS plate to obtain a sheet having a thickness of about 150  $\mu\text{m}$ .

Eight sheets of this sheet were put one on another and a copper foil having a thickness of 35  $\mu\text{m}$  was  
15 laminated to each of both surfaces of the resulting assembly, after which the assembly was pressed at a press temperature of 180°C at a press pressure of 40  $\text{kgf/cm}^2$  for 20 minutes so that the thickness of the resulting laminate might become 1 mm to fuse the assembly, thereby  
20 obtaining a laminate.

When this laminate was contacted with a solder at 260°C for 30 seconds, no abnormal phenomena such as peeling of copper foil, blistering and the like were observed. The laminate had a water absorption of 0.01%  
25 or less, an insulation resistance of  $4 \times 10^{16} \Omega$ , a dielectric constant at 1 MHz of 2.4 and a loss tangent at 1 MHz of 0.0005.

When this laminate was immersed in toluene and allowed to stand for 24 hours, swelling was confirmed but dissolution was not observed.

Thirteen sheets were put one on another, the  
5 resulting assembly was pressed at a press temperature of 180°C at a press pressure of 40 kgf/cm<sup>2</sup> for 20 minutes so that the thickness of the resulting laminate might become 1/16 inch to fuse the sheets, thereby obtaining a flame retardance test specimen. This test specimen was  
10 subjected to evaluation of flame retardance to judge the flame retardance as failure in the UL-94 specification.

### Example 3

A glass cloth substrate having a thickness of 0.1 mm was immersed in the cross-linkable norbornene  
15 resin composition solution obtained in Example 1 and then taken out. The glass cloth substrate impregnated with the cross-linkable norbornene resin composition was dried at 60°C for 20 minutes, and thereafter, allowed to stand at 150°C for ten minutes to obtain eight sheets of  
20 prepreg. About 40% by weight of this prepreg was the cross-linkable norbornene resin composition of this invention, and the thickness of the prepreg was about 110 µm.

The eight sheets of prepreg were put one on  
25 another and a copper foil having a thickness of 35 µm was laminated to each of both surfaces of the resulting assembly, and then the assembly was pressed at a press

temperature of 180°C at a press pressure of 40 kgf/cm<sup>2</sup> for 20 minutes so that the thickness of the resulting laminate might become 1 mm to fuse the sheets, thereby obtaining a laminate.

5                When this laminate was contacted with a solder at 260°C for 30 seconds, no abnormal phenomena such as peeling of copper foil, blistering and the like were observed. The laminate had a water absorption of 0.01%, an insulation resistance of  $1 \times 10^{17}\Omega$ , a dielectric  
10 constant at 1 MHz of 2.7 and a loss tangent at 1 MHz of 0.0009.

                 In the same manner as in Example 2, the flame retardance of the laminate was evaluated to judge the flame retardance as failure in the UL-94 specification.

15                When the above laminate was immersed in toluene for 24 hours and allowed to stand, swelling was confirmed but dissolution was not observed.

#### Example 4

                 In 80 parts by weight of toluene were dispersed  
20 20 parts by weight of a thermoplastic, hydrogenated, ring-opened norbornene resin (ZEONEX 280), 1 part by weight of dicumyl peroxide and 1 part by weight of trimethylolpropane trimethacrylate to obtain a uniform solution without causing precipitation and the like.



Example 5

The cross-linkable norbornene resin composition solution obtained in Example 4 was coated on a planished SUS plate so that the thickness of the coating film might become 750  $\mu\text{m}$ . The coated plate was allowed to stand at 60°C for 20 minutes and then at 120°C for 10 minutes to dry the coating film, and the coating film was peeled from the SUS plate to obtain a sheet having a thickness of about 150  $\mu\text{m}$ .

Eight sheets of this sheet were put one on another, and a copper foil having a thickness of 35  $\mu\text{m}$  was laminated to each of both surfaces of the resulting assembly, after which the assembly was pressed at a press temperature of 180°C at a press pressure of 40 kgf/cm<sup>2</sup> for 20 minutes so that the thickness of the resulting laminate might become 1 mm to fuse the sheets, thereby obtaining a laminate.

When this laminate was contacted with a solder at 260°C for 30 seconds, no abnormal phenomena such as peeling of foil, blistering and the like were observed. The laminate had a water absorption of 0.02%, an insulation resistance of  $2 \times 10^{16}\Omega$ , a dielectric constant at 1 MHz of 2.6 and a loss tangent at 1 MHz of 0.0007.

In the same manner as in Example 2, the laminate obtained was subjected to evaluation of flame retardance to judge the flame retardance as failure in the UL-94 specification.

When the laminate obtained was immersed in

toluene and allowed to stand for 24 hours, swelling was confirmed but dissolution was not observed.

#### Example 6

A glass cloth substrate having a thickness of 0.1 mm was immersed in the cross-linkable norbornene resin composition solution obtained in Example 5 and then taken out. The glass cloth substrate impregnated with the cross-linkable norbornene resin composition was dried at 60°C for 20 minutes, and thereafter allowed to stand at 150°C for ten minutes to obtain eight sheets of prepreg. About 40% by weight of the prepreg was the cross-linkable norbornene resin composition of this invention and the thickness was about 110  $\mu\text{m}$ .

The eight sheets of this prepreg were put one on another and a copper foil having a thickness of 35  $\mu\text{m}$  was laminated to each of both surfaces of the resulting assembly. The assembly was pressed at a press temperature of 180°C at a press pressure of 40 kgf/cm<sup>2</sup> for about 20 minutes so that the thickness of the resulting laminate might become 1 mm to fuse the sheets, thereby obtaining a laminate.

When this laminate was contacted with a solder at a temperature of 260°C for 30 seconds, no abnormal phenomena such as peeling of copper foil, blistering and the like were observed. The laminate had a water absorption of 0.03%, an insulation resistance of  $1 \times 10^{17} \Omega$ , a dielectric constant at 1 MHz of 2.8 and a loss

tangent at 1 MHz of 0.0011.

In the same manner as in Example 2, the laminate was subjected to evaluation of flame retardance to judge the flame retardance as failure in the UL-94  
5 specification.

When this laminate was immersed in toluene and allowed to stand for 24 hours, swelling was confirmed but dissolution was not observed.

#### Comparative Example 1

10 In 100 parts by weight of methyl ethyl ketone was dispersed and dissolved 70 parts by weight of a liquid epoxy type thermosetting composition having a high viscosity [to 100 parts by weight of Epikote 5046 manufactured by Yuka Shell (as a curable epoxy compound)  
15 were added 4 parts by weight of dicyandiamine as a curing agent, 14 parts by weight of dimethylformamide, and 0.2 part by weight of benzyldimethylamine as a curing coagent].

In this solution was immersed a glass cloth  
20 substrate having a thickness of 0.1 mm. The glass cloth substrate impregnated with the epoxy type thermosetting composition was dried at 60°C for ten minutes, and thereafter, allowed to stand at 150°C for ten minutes to obtain eight sheets of prepreg. About 50% by weight of  
25 this prepreg was the epoxy type thermosetting resin composition and the thickness thereof was about 130  $\mu$ m.

Eight sheets of this prepreg were put one on

another and a copper foil having a thickness of 35  $\mu\text{m}$  was laminated to each of both surfaces of the resulting assembly, after which the assembly was pressed at a press temperature of 180°C at a press pressure of 40 kgf/cm<sup>2</sup> for  
5 about 90 minutes so that the thickness of the resulting laminate might become 1 mm to fuse the sheets, thereby obtaining a laminate.

When this laminate was contacted with a solder at 260°C for 30 seconds, no abnormal phenomena such as  
10 peeling of foil, blistering and the like were observed. The laminate had a water absorption of 0.15%, an insulation resistance of  $1 \times 10^{15}\Omega$ , a dielectric constant at 1 MHz of 4.8 and a loss tangent at 1 MHz of 0.022. The water absorption, dielectric constant and loss tangent  
15 were not suitable as an insulating material.

#### Comparative Example 2

In 80 parts by weight of toluene were dispersed 20 parts by weight of a thermoplastic, hydrogenated, ring-opened norbornene resin (ZEONEX 280) and 1 part by  
20 weight of dicumyl peroxide to obtain a uniform solution without causing precipitation and the like.

This cross-linkable norbornene resin composition solution was coated on a planished SUS plate by a coating machine so that the thickness of the resulting  
25 coating film might become 750  $\mu\text{m}$ . The coated plate was allowed to stand at 60°C for 20 minutes and then at 120°C for ten minutes to be dried, after which the coating film

was peeled from the SUS plate to obtain a sheet having a thickness of about 150  $\mu\text{m}$ .

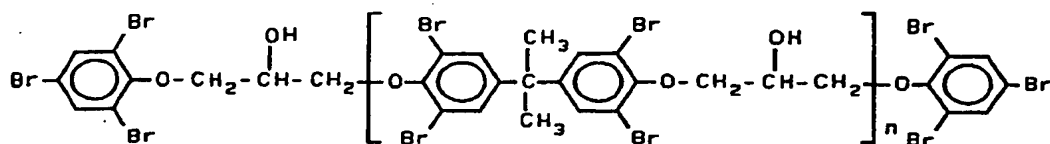
Eight sheets of this sheet were put one on another and a copper foil having a thickness of 35  $\mu\text{m}$  was  
 5 laminated to each of both surfaces of the resulting assembly after which the assembly was pressed at a press temperature of 180°C at a press pressure of 40 kgf/cm<sup>2</sup> for 20 minutes so that the thickness of the resulting laminate might become 1 mm to fuse the sheets, thereby  
 10 obtaining a laminate.

When this laminate was contacted with a solder at 260°C for 30 seconds, abnormal phenomena such as peeling of foil, blistering and the like were observed and distortion was further observed.

15 When this laminate was immersed in toluene and allowed to stand for 24 hours, almost all of the laminate was dissolved.

#### Example 7

In 80 parts by weight of toluene was dissolved  
 20 20 parts by weight of a brominated bisphenol type flame retarder (Plasafety EB-242 represented by the following formula:



and manufactured by MANAC INCORPORATED), and 75 parts by

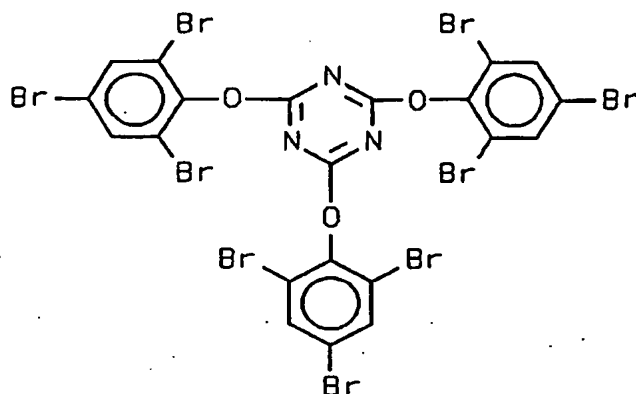
weight of this solution was mixed with 100 parts by weight of the resin solution obtained in Example 1 to obtain a uniform solution without causing precipitation, separation and the like.

5 Example 8

A laminate was prepared in the same manner as in Example 3 using the cross-linkable norbornene resin composition solution obtained in Example 7. When this laminate was contacted with a solder at 260°C for 30  
10 seconds, no abnormal phenomena such as peeling of foil, blistering and the like were observed. The laminate had a water absorption of 0.02%, an insulation resistance of  $5 \times 10^{16}\Omega$ , a dielectric constant at 1 MHz of 3.0 and a loss tangent at 1 MHz of 0.001. When this laminate was  
15 immersed in toluene and allowed to stand for 24 hours, dissolution was not observed. Also, the flame retardance was evaluated to be judged as V-0 in the UL-94 specification.

Example 9

20 In 80 parts by weight of toluene was dissolved 20 parts by weight of a brominated aromatic triazine type flame retarder (Pyroguard SR245 represented by the following formula:



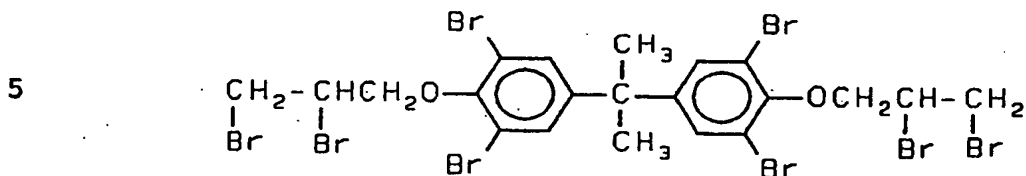
and manufactured by Daiichi Kogyo Seiyaku Co., Ltd.), and 75 parts by weight of this solution was mixed with 100 parts by weight of the resin solution obtained in Example 1 to obtain a uniform solution without causing precipitation, separation and the like.

#### Example 10

A laminate was prepared in the same manner as in Example 3 using the cross-linkable norbornene resin composition solution obtained in Example 9. When this laminate was contacted with a solder at 260°C for 30 seconds, no abnormal phenomena such as peeling of foil, blistering and the like were observed. The laminate had a water absorption of 0.02%, an insulation resistance of  $3 \times 10^{16} \Omega$ , a dielectric constant at 1 MHz of 3.0 and a loss tangent at 1 MHz of 0.001. When this laminate was immersed in toluene and allowed to stand for 24 hours, dissolution was not observed. Also, the flame retardance was evaluated to be judged as V-0 in the UL-94 specification.

Example 11

In 80 parts by weight of toluene was dissolved 20 parts by weight of a bisphenol type flame retarder (Firegaurd 3100 represented by the following formula:



and manufactured by TEIJIN CHEMICALS LTD.), and 75 parts by weight of this solution was mixed with 100 parts by weight of the resin solution obtained in Example 1 to obtain a uniform solution without causing precipitation, separation and the like.

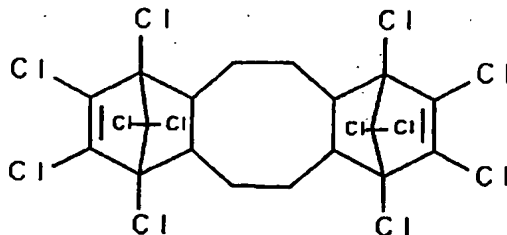
Example 12

A laminate was prepared in the same manner as in Example 3 using the cross-linkable norbornene resin composition solution obtained in Example 11. When this laminate was contacted with a solder at 260°C for 30 seconds, no abnormal phenomena such as peeling of foil, blistering and the like were observed. The laminate had a water absorption of 0.02%, an insulation resistance of  $3 \times 10^{16}\Omega$ , a dielectric constant at 1 MHz of 3.0 and a loss tangent at 1 MHz of 0.001. When this laminate was immersed in toluene and allowed to stand for 24 hours, dissolution was not observed. Also, the flame retardance was evaluated to be judged as V-2 in the UL-94 specification.



Comparative Example 3

In 80 parts by weight of toluene was dissolved  
20 parts by weight of cyclic chloroparaffin type flame  
retarder (Dechloran Plus represented by the following  
5 formula:

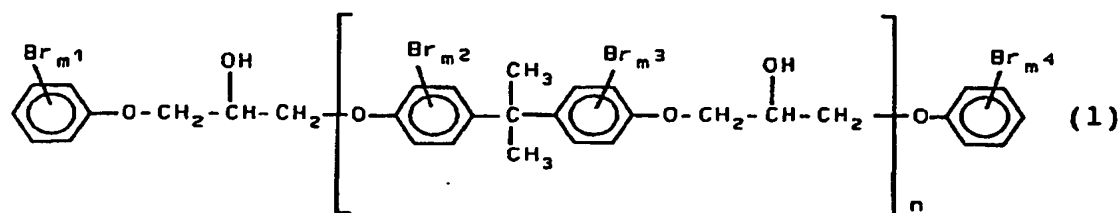


and manufactured by Occidental Chemical Corporation), and  
75 parts by weight of this solution was mixed with 100  
parts by weight of the resin solution obtained in Example  
10 1. However, the two were not dissolved in each other and  
when the mixture was allowed to stand for one week,  
precipitation was caused.

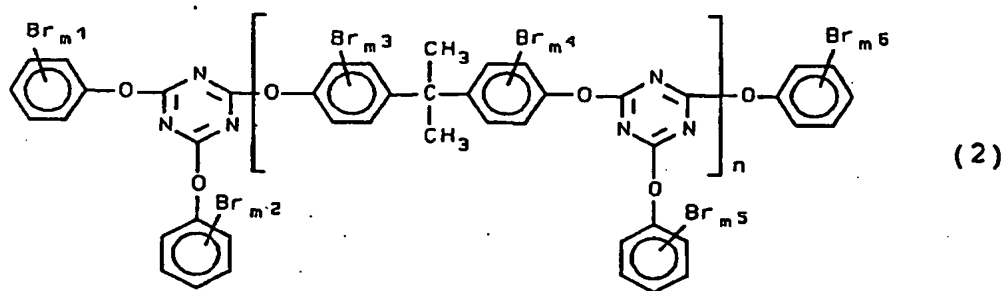
Cross-linked molded articles obtained from the  
cross-linkable norbornene resin composition of this  
15 invention are excellent in heat resistance, chemical  
resistance, moisture resistance, water resistance and  
electric characteristics and, when contacted with a  
solder at 260°C for 30 seconds, do not cause peeling of  
foil, blistering and the like and are hardly dissolved in  
20 toluene. Said molded articles are excellent particularly  
in heat resistance and chemical resistance and useful as  
a radiofrequency circuit board substrate or the like.

WHAT IS CLAIMED IS:

1. A uniform, cross-linkable norbornene resin composition comprising 100 parts by weight of a thermoplastic, hydrogenated, ring-opened norbornene resin having dispersed therein 0.001 to 30 parts by weight of an organic peroxide and 0.1 to 10 parts by weight, per part by weight of the organic peroxide, of a cross-linking coagent.
2. The cross-linkable norbornene resin composition according to Claim 1, wherein 1 to 30 parts by weight of the organic peroxide is dispersed in 100 parts by weight of the thermoplastic, hydrogenated, ring-opened norbornene resin.
3. The cross-linkable norbornene resin composition according to Claim 1, which further contains 5 to 150 parts by weight of a flame retarder represented by the general formula (1):

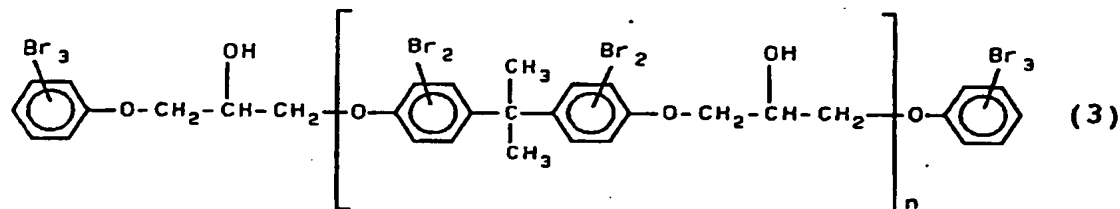


wherein  $n$ ,  $m^1$ ,  $m^2$ ,  $m^3$  and  $m^4$  are integers and satisfy  $n \geq 0$ ,  $1 \leq m^1 \leq 5$ ,  $1 \leq m^2 \leq 4$ ,  $1 \leq m^3 \leq 4$  and  $1 \leq m^4 \leq 5$  or the general formula (2):



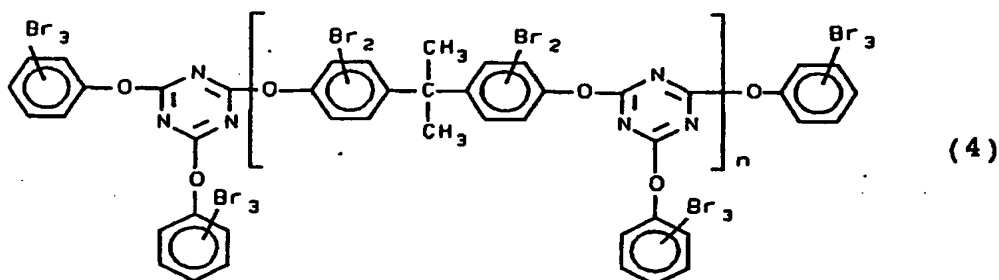
wherein  $n$ ,  $m^1$ ,  $m^2$ ,  $m^3$ ,  $m^4$ ,  $m^5$  and  $m^6$  are integers and satisfy  $n \geq 0$ ,  $1 \leq m^1 \leq 5$ ,  $1 \leq m^2 \leq 5$ ,  $1 \leq m^3 \leq 4$ ,  $1 \leq m^4 \leq 4$ ,  $1 \leq m^5 \leq 5$  and  $1 \leq m^6 \leq 5$ , per 100 parts by weight of the thermoplastic, hydrogenated, ring-opened norbornene resin.

4. The cross-linkable norbornene resin composition according to Claim 3, wherein the flame retarder is a compound represented by the general formula (3):



wherein  $n$  is an integer of 0 or more.

5. The cross-linkable norbornene resin composition according to Claim 3, wherein the flame retarder is a compound represented by the general formula (4):



wherein n is an integer of 0 or more.

6. The cross-linkable norbornene resin composition according to Claim 1, wherein the hydrogenation degree of the hydrogenated ring-opened norbornene resin is 90% or more.

7. The cross-linkable norbornene resin composition according to Claim 1, wherein the cross-linking coagent is an allyl type cross-linking coagent or a methacrylate type cross-linking coagent.

8. The cross-linkable norbornene resin composition according to Claim 7, wherein the cross-linking coagent is selected from the group consisting of diallyl phthalate, triallyl cyanurate, triallyl isocyanurate, ethylene glycol dimethacrylate, and trimethylolpropane trimethacrylate.

9. A cross-linkable molded article consisting essentially of the cross-linkable norbornene resin composition according to Claim 1.

10. The cross-linkable molded article according to Claim 9, which is a film or sheet.

11. The cross-linkable molded article according to Claim 10, wherein the film or sheet is prepared by dissolving the cross-linkable norbornene resin composition in a solvent and then casting the solution.

12. The cross-linkable molded article according to Claim 9, which is a prepreg.

13. The cross-linkable molded article according to Claim 12, wherein the prepreg is prepared by dissolving

the cross-linkable norbornene resin in a solvent and then impregnating a substrate with the solution.

14. A cross-linked molded article prepared by cross-linking the cross-linkable molded article according to Claim 9.

15. The cross-linked molded article according to Claim 14, wherein the cross-linking is effected by heating at 80 to 350°C.

16. The cross-linked molded article according to Claim 15, wherein the heating is effected for 1 to 120 minutes.

17. The cross-linked molded article according to Claim 14, wherein a plurality of the cross-linked molded articles are put one on another and then cross-linked to form an integrated molded article.

18. The cross-linked molded article according to Claim 14, which has a flame retardance of V-2 or better as evaluated in accordance with the UL-94 specification.

19. The cross-linked molded article according to Claim 18, wherein the flame retardance is V-0.

ABSTRACT OF THE DISCLOSURE

A cross-linked molded article which is excellent in chemical resistance, moisture resistance, water resistance and electric characteristics, also excellent in heat resistance to such an extent that when contacted with a solder at 260°C for 30 seconds it does not cause peeling of a foil laminated nor blistering, and useful as a radiofrequency circuit board substrate, which molded article is prepared by dispersing in a solvent 100 parts by weight of a thermoplastic, hydrogenated, ring-opened norbornene resin, 0.001 to 30 parts by weight of an organic peroxide such as  $\alpha, \alpha'$ -bis(t-butylperoxy-m-isopropyl)benzene or the like, 0.1 to 10 parts by weight, per part by weight of the organic peroxide, of a cross-linking coagent such as diallyl phthalate or the like to prepare a uniformly compounded composition, molding the composition into a sheet or the like by a solution-casting method or the like and then heating the molded article to cross-linking the same.

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## CLAIMS

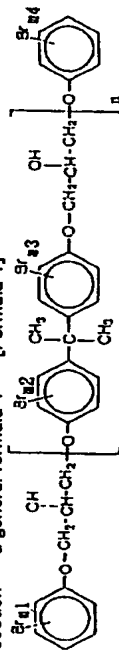
[Claim(s)]

[Claim 1] The uniform cross-linking norbornene system resin constituent which distributes the bridge formation assistant 0.1 – 10 weight sections, and changes to organic peroxide 0.001 – 30 weight sections, and the organic peroxide 1 weight section to the thermoplastic hydrogenation ring breakage norbornene system resin 100 weight section.

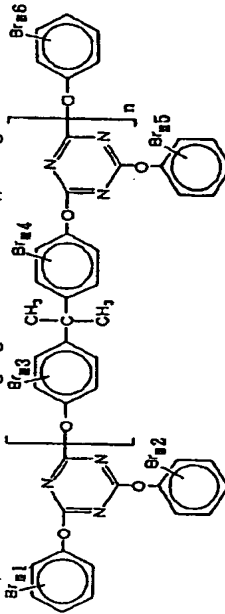
[Claim 2] The cross-linking norbornene system resin constituent according to claim 1 whose rate of hydrogenation of this hydrogenation ring breakage norbornene system resin is 90% or more.

**[Claim 3] Claim 1 this whose bridge formation assistant is an allyl compound system bridge formation assistant or a methacrylate system bridge formation assistant, or a cross-linking norbornene system resin constituent given in two.**

[Claim 4] the thermoplastic hydrogenation ring breakage norbornene system resin 100 weight section -- a general formula 1 -- [Formula 1]



( $n, m_1, m_2, m_3$ , and  $m_4$  being integers, and they being  $n \geq 0, 1 \leq m_1 \leq 5, 1 \leq m_2 \leq 4, 1 \leq m_3 \leq 4$ , and  $1 \leq m_4 \leq 5$  among a general formula 1), or a general formula 2 -- [Formula 2]



( $n, m_1, m_2, m_3, m_4, m_5$ , and  $m_6$  are integers among a general formula 2.)  $n \geq 0$  and  $1 \leq m - \{ \leq 5, 1 \leq m_2 \leq 5, 1 \leq m_3 \leq 4$ , and  $1 \leq m - 4 \leq 4, 1 \leq m_5 \leq 5$ , and  $1 \leq m_6 \leq 5$  -- it is -- claims 1 and 2 which carry out 5-150 weight section addition of the flame retarder expressed, and change, or a cross-linking norbornene system resin constituent given in three.

[Claim 5] Claims 1, 2, and 3 or cross-linking mold goods which consists of a cross-linking norbornene system resin constituent given in four.

[Claim 6] A film or cross-linking mold goods according to claim 5 which is sheets.

[Claim 7] Cross-linking mold goods according to claim 5 which are prepeg.

[Claim 8] Claims 5 and 6 or bridge formation mold goods over which heat cross-linking mold goods given in seven, and they are made to construct a bridge.

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## DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the cross-linking norbornene system resin constituent excellent in electric insulation, the cross-linking mold goods which change, and bridge formation mold goods.

[0002]

[Description of the Prior Art] With the advance of a technique, the demand of improvement in the speed of data processing, a raise in reliance, densification, etc., etc. increases, and, as for circuits, such as precision mechanical equipments, such as a computer and a transmitter, high performance-ization, such as multilayering of the circuit board, high-degree-of-accuracy-izing, and detailed-izing, is progressing.

[0003] Conventionally, as such the circuit board, phenol resin, an epoxy resin, polyimide resin, the fluororesin, or the polybutadiene resin is used, and it is improved according to an advance of a technique (JP.60-84317.A, JP.60-258233.A, JP.60-202130.A, JP.3-37258.A, JP.3-55237.A, JP.3-168258.A, JP.3-275760.A, etc.).

[0004] However, when difficulty was usually in an electrical property since 4.0 or more and a dielectric dissipation factor have the dielectric constant as high as 0.01 or more, and these resin was used for the circuit board etc., improvement in the speed of data processing and a raise in reliance were difficult for thermosetting resin, such as phenol resin, an epoxy resin, and polyimide resin. On the other hand, since the laminate of prepreg using thermoplastics, such as a fluororesin and a polybutadiene resin, was inferior to thermal resistance, a crack and exfoliation might arise, the dimensional stability of the laminate was also bad on the occasion of pewter attachment etc., and it was difficult [to multilayer] for it.

[0005] The method of improving thermal resistance, solvent resistance, etc. is proposed from carrying out organic peroxide bridge formation of the thermoplastic norbornene system resin recently. For example, by the approach indicated by JP.62-34924.A, after grinding after kneading resin and a bridge formation assistant, carrying out impregnation of the organic peroxide solution to it and removing a solvent, the approach of carrying out press forming and constructing a bridge is indicated. However, in such a procedure, a process is complicated and there is a problem that organic peroxide does not necessarily distribute to homogeneity, the top where effectiveness is bad. Moreover, the thermoplastic norbornene system resin currently indicated in this official report was a norbornene system monomer and the copolymer of ethylene, when it was going to construct the bridge with organic peroxide by this approach, lowering of the molecular weight by disassembly of a polymer often produced the hydrogenation ring breakage norbornene system resin which is not indicated, and it became clear that thermal resistance required for pewter attachment etc. was not obtained.

[0006] moreover, to JP.2-255848.A Although constructing a bridge using organic peroxide is indicated, the resin constituent which blended the styrene system copolymer of the alpha olefin system copolymer of amorphism nature or low crystallinity and amorphism nature, or low crystallinity with thermoplastic norbornene system resin including hydrogenation ring breakage norbornene system resin. There is no example over which the bridge was concretely constructed

about hydrogenation ring breakage norbornene system resin, and constructing a bridge using organic peroxide in the hydrogenation ring breakage norbornene system resin which does not blend these special resin is not indicated. Furthermore, although the approach of blending a flame retarder is indicated in this official report after blending the approach, resin, and organic peroxide which blend organic peroxide, a bridge formation assistant, and a flame retarder with such a resin constituent, and construct a bridge and constructing a bridge By the approach of blending a flame retarder after bridge formation, when using for the laminate of prepreg etc., it is hard to distribute a flame retarder to homogeneity. When there is a problem of not being practical, and a flame retarder is blended before bridge formation and only hydrogenation ring breakage norbornene system resin is used as resin in the flame retarder illustrated by this official report, there was a problem from which it denaturalizes with organic peroxide and sufficient fire retardancy is not acquired that there were some which are not distributed to homogeneity.

[0007]

[Problem(s) to be Solved by the Invention] Then, this invention persons were excellent in thermal resistance, find out that a bridge can be constructed without producing disassembly of a polymerization band if thermoplastic hydrogenation ring breakage norbornene system resin is made to distribute organic peroxide and a bridge formation place agent to homogeneity as a result of wholeheartedly research for the purpose of development of the mold goods which consist of a dielectric constant and the low resin of a dielectric dissipation factor, and came to complete this invention.

[0008]

[Means for Solving the Problem] In this way, according to this invention, the cross-linking mold goods which consist of the uniform cross-linking norbornene system resin constituent and this cross-linking norbornene system resin constituent which distribute the bridge formation assistant 0.1 - 10 weight sections, and change to organic peroxide 0.001 - 30 weight sections, and the organic peroxide 1 weight section to the thermoplastic hydrogenation ring breakage norbornene system resin 100 weight section, and the bridge formation mold goods over which heat these cross-linking mold goods and they are made to construct a bridge are offered.

[0009] (Thermoplastic hydrogenation ring breakage norbornene system resin) In JP.3-14882.A, JP.3-122137.A, etc., the thermoplastic hydrogenation ring breakage norbornene system resin used for this invention is well-known resin, and, specifically, is the hydrogenation object of the ring-opening-polymerization object of a norbornene system monomer.

[0010] A norbornene system monomer is also a monomer well-known at the above-mentioned official report, JP.2-227424.A, JP.2-276842.A, etc. For example, norbornene, its alkyl, alkylidene, an aromatic substitution derivative and these permutations, or the halogen of an unsubstituted olefin, A hydroxyl group, an ester group, an alkoxy group, a cyano group, an amide group, an imide radical, Polar-group substitution products, for example, 2-norbornene, such as a silyl radical, 5-methyl-2-norbornene, 5 and 5-dimethyl-2-norbornene, 5-ethyl-2-norbornene, 5-butyl-2-norbornene, 5-ethylidene-2-norbornene, 5-methoxycarbonyl-2-norbornene, 5-cyano-2-norbornene, 5-methyl-5-methoxycarbonyl-2-norbornene, 5-phenyl-2-norbornene, 5-octadecyl-2-norbornene, methyl-2-norbornene, 5-hexyl-2-norbornene, 5-octyl-2-norbornene, 5-octadecyl-2-norbornene, etc.; The monomer which one or more cyclopentadienes added to norbornene, The same derivative and same substitution product as the above, 1 [for example, 1, 4, 5, 8-dimethano - 1, 2, 3, 4, 4a, 5, 8, 8a-2, 3-cyclopentadieno naphthalene, The 6-methyl - 1, 4, 5, 8-dimethano - 1, 4a [4], 5, 6, 7, 8, and 8a-octahydronaphthalene, 1, 4, 5, 10, 8, 9-trimethano - 1, 2, 3, 4a [4], 5a [5], 6, 9a [9], 10, and 10a-dodecahydronalium - 2, 3-cyclopentadieno anthracene, etc.; A monomer, the same derivative and same substitution product as the above of the polycyclic structure which is the polymer of a cyclopentadiene, For example, a dicyclopentadiene, 2, a 3-dihydrodicyclopentadiene, etc.; The addition product of a cyclopentadiene, a tetrahydro indene, etc.; The same derivative and same substitution product as the above, 1 [for example, 1, 4-methano - 1, 4, 4a, 4b, 5, 8, 8a, a 9a-octahydro fluorene, 5, the 8-methano - 1, 2, 3, 4, 4a, 5 and 8, 8a-octahydro - 2, 3-cyclopentadieno naphthalene, etc.; etc. — it is mentioned.

[0011] A well-known approach may be used for the ring opening polymerization of a norbornene



system monomer, and it may be copolymerized with other copolymerizable monomers if needed. By the well-known approach, a polymer may be denatured using an organic silicon compound and a partial saturation epoxy monomer with the radical in which alpha and beta-unsaturated carboxylic acid and/or its derivative, a styrene system hydrocarbon, an olefin system unsaturated bond, and hydrolysis are possible by JP 3-95235A etc. It considers as thermoplastic hydrogenation ring breakage norbornene system resin by hydrogenating these resin. You may denaturalize resin after hydrogenation.

[0012] GPC (gel purge ESHON chromatography) to which the molecular weight of hydrogenation reduced norbornene system resin uses a cyclohexane as a solvent — the polystyrene reduced property measured by law — it is 10,000-200,000 — desirable — 20,000,000 — it is 25,000-50,000 more preferably. When number-average molecular weight is too small, a mechanical strength is inferior, and if too large, a moldability will worsen. Moreover, the rate of hydrogenation is 90% or more more preferably 95% or more in order to raise heat-resistant degradation nature and photodegradation-proof nature.

[0013] as long as it can distribute at homogeneity to the hydrogenation ring breakage norbornone system resin used by this invention — a request — antioxidants, such as a phenol system and the Lynn system; Heat deterioration inhibitors, such as a phenol system; UV stabilizer, such as a benzophenone system; Antistatic agents, such as an amine system; Lubricant, such as ester of fatty alcohol, partial ester of polyhydric alcohol, and the partial ether; etc. — various additives may be added.

[0014] (Organic peroxide) The organic peroxide used for this invention It is not limited especially but is easy to be well-known at JP.82-34924.A, etc. For example, t-butyl hydroperoxide, p-menthaphthene hydroperoxide, Hydroperoxide, such as cumene hydroperoxide; JIKUMIN peroxide, Dialkyl peroxide, such as t-butyl cumin peroxide, alpha, and alpha-bis(tert-butyl peroxide-m-isopropyl) benzene; Dipropionyl peroxide, Diacyl peroxide, such as benzoyl peroxide; 2, 2, the 5-dimethyl-2, 5-di-tert-butyl peroxide hexane, 2, the 5-dimethyl-2, 5-di-tert-butyl peroxide hexyne - Peroxy ketals, such as 3, 1, and 3-Jl (t-butyl PAOKI seesaw propyl) benzene; T-butyl peroxyacetate, peroxy ester, such as t-butyl peroxybenzoate; Ketone peroxide, such as peroxyl cull BONATO and Jl (isopropyl peroxyl) dicarbonate; etc. — it is mentioned.

[0015] The bridge formation assistant used for this invention is not limited especially, either, but it is easy to be well-known [ an assistant ] at JP, 62-34924 A etc. (Bridge formation assistant). Oxime nitroso bridge formation assistants, such as quinonedioxime, benzoquinone dioxime, and p-nitrosophenol; Maleimide system bridge formation assistants, such as N and N-m-phenylene bismaleimide; Diallyl phthalate, Allyl compound system bridge formation assistants, such as a triaryl SHIANU rate and triallyl isocyanurate; Ethylene glycol dimethacrylate, methacrylate system bridge formation assistants, such as trimethylolpropanetrimethacrylate; Vinyl system bridge formation assistants, such as vinyltoluene, ethyl vinylbenzene, and a divinylbenzene; etc. - it is illustrated. Especially, an allyl compound system bridge formation assistant and a methacrylate system bridge formation assistant are easy to distribute homogeneity, and desirable.

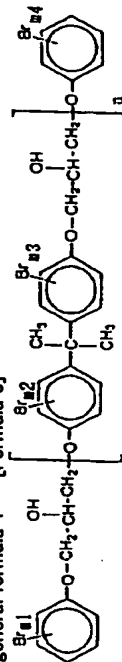
**[0016]** (Cross-linking norbornene system resin constituent) The cross-linking norbornene system resin constituent of this invention is a uniform constituent which adds organic peroxide and a bridge formation assistant to thermoplastic hydrogenation ring breakage norbornene system resin, and grows into it.

[0017] If there are too few additions of organic peroxide, since bridge formation will stop being able to happen easily, the organic peroxide more than 1 weight section is preferably added especially more than the 0.05 weight section more than the 0.01 weight section more than the 0.001 weight section to the thermoplastic hydrogenation ring breakage norbornene system resin 100 weight section. since [ moreover, ] the electrical property of the resin which constructed the bridge when there were too many additions of organic peroxide, a water resisting property, moisture resistance, etc. fall — the thermoplastic hydrogenation ring breakage norbornene system resin 100 weight section — receiving — 30 weight sections — desirable — 15 weight sections — more — desirable — 10 weight sections — organic peroxide is added so that 5

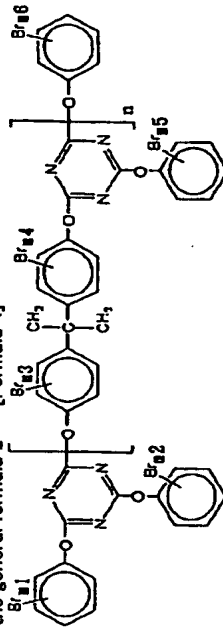
weight sections may not be exceeded especially preferably.

[0018] moreover, the addition of a bridge formation assistant — the organic peroxide 1 weight section — receiving — 0.1 – 10 weight section — it is 0.2 – 5 weight section preferably. Since bridge formation cannot take place easily, hydrogenation ring breakage norbornene system resin will decompose and molecular weight will fall if there are too few additions of a bridge formation assistant, thermal resistance required for power attachment is not obtained. Since the electrical property of the resin which constructed the bridge when there were too many additions of a bridge formation assistant, a water resisting property, moisture resistance, etc. fall, it is not desirable.

[0019] Furthermore, in order to raise the fire retardancy of the bridge formation mold goods of this invention, it is desirable to make the norbornene system resin constituent of this invention a flame retarder to homogeneity. As for the flame retarder used in this invention, what homogeneity can be distributed as a resin constituent, sets at the condition of having blended as a resin constituent and, and the process of crosslinking reaction, and does not denaturalize [ does not decompose and ] and deteriorate with organic peroxide is desirable, concrete — a general formula 1 — [Formula 3]



$(n, m_1, m_2, m_3, \text{ and } m_4 \text{ are integers among a general formula 1.) } n \geq 0, 1 \leq m_1 \leq 5, \text{ and } 1 \leq m_2 = 2 \leq 4, 1 \leq m_3 \leq 4, \text{ and } 1 \leq m_4 \leq 5 \text{ --- desirable --- } 2 \leq m_1 \leq 4 \text{ and } 2 \leq m_2 = 2 \leq 3, 2 \leq m_3 \leq 3, \text{ and } 2 \leq m_4 \leq 4 \text{ --- especially --- desirable --- } m_1 = 3 \text{ and } m_2 = 2, m_3 = 2, \text{ and } m_4 = 3 \text{ --- or the general formula 2 --- [Formula 4]}$



( $n$ ,  $m$ 1,  $m$ 2,  $m$ 3,  $m$ 4,  $m$ 5, and  $m$ 6 are integers among a general formula 2.)  $n \geq 0$  and  $1 \leq m - 1 \leq 5$ ,  $1 \leq m2 \leq 5$ ,  $1 \leq m3 \leq 4$ , and  $1 \leq m - 4 \leq 4$ ,  $1 \leq m5 \leq 5$ , and  $1 \leq m6 \leq 5$ .  $1 \leq m - 1$  preferably  $\leq 4$ ,  $2 \leq m2 \leq 4$ ,  $2 \leq m3 \leq 3$ , and  $2 \leq m - 4 \leq 3$ , and  $2 \leq m5 \leq 4$ , and  $2 \leq m6 \leq 4$  — especially — desirable —  $m - 1 = 3$ ,  $m2 = 3$ ,  $m3 = 2$ , and  $m - 4 = 2$ ,  $m5 = 3$ , and  $m6 = 3$  — it is — the flame retarder expressed can distribute to homogeneity, and it does not decompose, denaturalize and deteriorate with organic peroxide, an addition — the hydrogenation ring breakage norbomene system resin 100 weight section — receiving — the 5 - 150 weight section — desirable — the 20 - 140 weight section — it is the 40 - 120 weight section especially preferably.

[0020] Especially the approach of distributing a flame retarder at homogeneity organic peroxide, a bridge formation assistant, and if needed to hydrogenation ring breakage norbornene system resin has the approach of it not being limited, for example, making it mixing and distributing in ring breakage resin solution, and removing a solvent, the approach of mixing and distributing after ring breakage resin has fused, etc. Especially if the solvent of ring breakage resin also dissolves ring breakage resin, it will not be limited, for example, toluene, a xylene, ethylbenzene, a chlorobenzene, etc. can be used. In addition, in the approach of making carry out melting of the ring breakage resin, and mixing and distributing organic peroxide etc., it is the temperature which does not construct a bridge, and melting, mixing, and distribution must be able to be performed and this approach cannot be used depending on the combination of ring breakage resin, organic

peroxide, and a bridge formation assistant. When heating in order to remove a solvent also in the approach of mixing and distributing in a ring breakage resin solution, it is necessary to carry out temperature setting out so that bridge formation may not take place.

[0021] (Cross-linking mold goods) In this invention, after fabricating a cross-linking norbornene system resin constituent, a bridge is made to construct and cross-linking mold goods are obtained.

[0022] The temperature which dissolves in a solvent, and fabricates or does not construct a bridge, or a bridge formation rate fuses and fabricates the approach of fabricating a cross-linking norbornene system resin constituent at temperature late enough so that aggravation of a moldability may not take place according to bridge formation in the middle of shaping. As a solvent, the solvent which dissolves the above-mentioned hydrogenation ring breakage norbornene system resin is used. Generally it dissolves in a solvent and fabricates.

[0023] The cross-linking norbornene system resin constituent which dissolved in the solvent is specifically cast, a solvent is removed, and it fabricates on a sheet or a film, or impregnation is carried out to base materials, such as letter base materials of a cross, such as glass fabrics, an aramid cross, a polyester cross, and a nylon cross, the same mat-like base material of construction material as these, a nonwoven fabric, kraft paper, and linter paper, and it fabricates. Prepreg is illustrated as cross-linking mold goods which carried out impregnation of the resin constituent to the base material.

[0024] (Bridge formation) In this invention, are independent or carry out a laminating, and heat cross-linking mold goods more than constant temperature, they are made to construct a bridge, and bridge formation mold goods are obtained. Although the temperature which produces crosslinking reaction is decided mainly with the combination of organic peroxide and a bridge formation assistant, generally it constructs a bridge 120 degrees C - 300 degrees C preferably 80-350 degrees C by heating in temperature of 150-250 degrees C still more preferably.

Moreover, generally [ it is desirable to make it about 4 times of the half-life of organic peroxide, and ] bridge formation time amount is 20 - 60 minutes still more preferably preferably for 10 to 90 minutes for 5 to 120 minutes. When carrying out the laminating of the cross-linking mold goods and constructing a bridge, thermal melting arrival and bridge formation take place between each class, and the bridge formation mold goods of one are obtained.

[0025] (Bridge formation mold goods) As bridge formation mold goods of this invention, a laminate, the circuit board, an interlayer insulation film, the film for damp-proof-course shaping, etc. are illustrated as a thing made to construct a bridge.

[0026] For 0.03% or less and insulation resistance, the dielectric constant in 1015-1017ohm, and 1MHz and a dielectric dissipation factor are [ water absorption ] 2.0-2.5, and 0.0001-0.0007, respectively, and the bridge formation mold goods of this invention are usually excellent in the water resisting property and the electrical property compared with the conventional thermosetting resin production type article. On the other hand, thermal resistance is equivalent to the conventional thermosetting resin production type article, and even if it contacts a 280-degree C pewter to the laminate which carried out the laminating of the copper foil for 30 seconds, the above, such as exfoliation of copper foil and generating of blistering, is not accepted. The laminate which is the bridge formation mold goods of these things to this invention is desirable also as the circuit board.

[0027] Moreover, the bridge formation mold goods of this invention have the thing excellent in fire retardancy, and the desirable thing which specifically shows the fire retardancy which was superior to V-2 or it in UL-94 specification, what shows the fire retardancy of V-1 or V-0 is more desirable, and especially its thing that shows the fire retardancy of V-0 is desirable. What is necessary is just to use the cross-linking norbornene system resin constituent containing the above flame retarders, in order to obtain such cross-linking mold goods.

[0028] (Prepreg) In the prepreg which is one of the examples of the cross-linking mold goods of this invention, especially the base material is not limited but, generally can use letter base materials of a cross, such as glass fabrics used as prepreg and a substrate, an aramid cross, a polyester cross, and a nylon cross, the same mat-like base material of construction material as these, a nonwoven fabric, kraft paper, linter paper, etc.

[0029] After manufacture of the prepreg using the cross-linking norbornene system resin constituent of this invention makes about 5 - 50 % of the weight of concentration dissolve a cross-linking norbornene system resin constituent into solvents, such as toluene, a cyclohexane, and a xylene, and carries out impregnation of the base material into the solution that what is necessary is just to follow a conventional method, it is made to dry and it should just remove a solvent. As for prepreg, generally, it is desirable to make it become the thickness of about 50-500 micrometers.

[0030] (Sheet) Especially the method of manufacturing the sheet which is one of the examples of the cross-linking mold goods of this invention is not limited. Generally the casting method is used. For example, in solvents, such as toluene, a xylene, and a cyclohexane, it dissolves and the cross-linking norbornene system resin constituent of this invention is distributed so that it may become about 5 - 50 % of the weight of concentration, and it casts or applies on a smooth side, desiccation etc. removes a solvent, it exfoliates from a smooth side, and a sheet is obtained. What is necessary is it being desirable choosing an approach's twisting foaming by rapid desiccation, when desiccation removes a solvent's, for example, raising temperature and making it just fully volatilize a solvent, after volatilizing the extent solvent which is low temperature. What is necessary is just to use a metal plate, a carrier film made of resin, etc. which carried out mirror plane processing as a smooth side. When using the carrier film made of resin, the solvent which it is careful of and is used for the solvent resistance of the raw material of a carrier film and thermal resistance, and desiccation conditions must be decided. Generally the sheet obtained by the casting method has the thickness of 10 micrometers - about 1mm. these sheets construct a bridge - an interlayer insulation film and a damp proof course - a characteristic - it can use as a \*\* film etc. Moreover, it can also use for manufacture of the laminate indicated below.

[0031] (Laminate) The laminate which is one of the examples of the bridge formation mold goods of this invention accumulates the above-mentioned prepreg and/or the sheet non-constructed a bridge, carries out heating compression molding, and is made into required thickness by carrying out bridge formation and thermal melting arrival. In using a laminate as the circuit board, the laminating of the conductive layer for wiring which consists of a metallic foil etc. is carried out, or it forms a circuit by surface etching processing etc. It not only carries out a laminating to the outer surface of the laminate which is a finished product, but the laminating of the conductive layer for wiring may be carried out to the interior of a laminate by the object etc. For the curvature prevention at the time of fabricating, such as etching processing, it is desirable to combine and to carry out a laminating to the object for vertical. For example, beyond the temperature according to the cross-linking norbornene system resin using the front face of the piled-up prepreg and/or the piled-up sheet that carries out thermal melting arrival, it usually heats at about 150-300 degrees C, about two 30 - 80 kgf/cm is pressurized, bridge formation and thermal melting arrival are carried out between each class, and a laminate is obtained.

[0032]

[Example] An example and the example of a comparison are raised to below, and this invention is explained still more concretely. In addition, insulation resistance, a dielectric constant, a dielectric dissipation factor, and water absorption are JIS. C It measured by 8481 and the following approaches estimated fire retardancy according to UL-94 specification.

[0033] Using a test piece with a thickness of 1/16 inch, the upper bed of a test piece is stopped by the clamp, a test piece is fixed vertically, and the place of 12 inches is covered with cotton under a test piece. The fire of a gas burner is applied to the soffit of a test piece for 10 seconds, the 1st burning time of a test piece is measured, if fire goes out, the fire of a gas burner will be again applied to a soffit for 10 seconds, and the 2nd burning time of a test piece is measured. When setting total of ten data of the 1st burning time and the 2nd burning time to T about five test pieces and setting the greatest data to M, it was judged as V-0, V-1, V-2, and a rejection by the following criteria.

V-0: The melt which T did not blaze up to the clamp 10 or less seconds, and flame attached [ 50 or less seconds and M ] falls, and cotton is not lit.

V-1: The melt which T did not blaze up to the clamp 30 or less seconds, and flame attached

[ 250 or less seconds and M ] falls, and cotton is not lit.

V-2: The melt which flame attached [ 250 or less seconds and M ] although T did not blaze up to the clamp 30 or less seconds fall, and cotton was lit.

Rejection: Don't satisfy the requirements of above V-0, V-1, and V-2.

[0034] When the example 1 hydrogenation ring breakage norbornene system resin (ZEONEX 280, Nippon Zeon Co., Ltd. make, glass-transition-temperature [ of 140 degrees C ], number-average-molecular-weight 28,000 [ about ], 99.7% or more of rates of hydrogenation) 20 weight section, the alpha and alpha-bis(tert-butyl peroxide-m-isopropyl) benzene 1 weight section, and the diallyl phthalate 1 weight section were distributed in the toluene 80 weight section, precipitation etc. was not produced but it became a uniform solution.

[0035] It applied so that it might become 750 micrometers in thickness on the SUS plate which made the mirror plane to the cross-linking norbornene system resin constituent solution obtained in the example 2 example 1 using the coater. It was left at 120 more degrees C for 10 minutes, and was made to dry for 20 minutes at 60 degrees C. Then, the formed sheet was removed from the SUS plate. The thickness of the obtained sheet was about 150 micrometers.

[0036] The laminating of these eight sheets was carried out, the laminating of the 35-micrometer copper foil was further carried out to both sides, it pressed for 20 minutes, and thermal melting arrival was carried out and the laminate was obtained so that the press temperature of 180 degrees C and press \*\* 40 kgf/cm<sup>2</sup> might make 1mm in thickness.

[0037] Even if this laminate contacted the 260-degree C pewter for 30 seconds, the above, such as exfoliation of copper foil and blistering, was not accepted, but water absorption was [ the dielectric constant in 4x1016 ohms and 1MHz and the dielectric dissipation factor of insulation resistance ] 2.4 and 0.0005 0.01% or less, respectively.

[0038] The dissolution was not accepted, although swelling was accepted when it was immersed in toluene and this laminate was left for 24 hours.

[0039] Moreover, the laminating of the 13 sheets was carried out, it pressed for 20 minutes, and thermal melting arrival was carried out and the test piece for a fire-resistant trial was obtained so that the press temperature of 180 degrees C and press \*\* 40 kgf/cm<sup>2</sup> might make 1/16 inch in thickness. When fire retardancy was evaluated using this test piece, in UL-94 specification, it was a rejection.

[0040] In the cross-linking norbornene system resin constituent solution obtained in the example 3 example 1, it was immersed and the glass KURORU base material with a thickness of 0.1mm was taken out. After drying the glass-fabrics base material to which impregnation of the cross-linking norbornene system resin constituent was carried out at 60 degrees C for 20 minutes, it was left for 10 minutes at 150 degrees C, and eight prepreps were obtained. 40% of the weight of this prepreg was the cross-linking mold goods of this invention, and thickness was about 110 micrometers.

[0041] The laminating of these eight prepreps was carried out, the laminating of the 35-micrometer copper foil was further carried out to both sides, it pressed for 20 minutes, and thermal melting arrival was carried out and the laminate was obtained so that the press temperature of 180 degrees C and press \*\* 40 kgf/cm<sup>2</sup> might make 1mm in thickness.

[0042] Even if this laminate contacted the 260-degree C pewter for 30 seconds, the above, such as exfoliation of copper foil and blistering, was not accepted, but water absorption was [ the dielectric constant in 1x1017 ohms and 1MHz and the dielectric dissipation factor of insulation resistance ] 2.7 and 0.0009 0.01%, respectively.

[0043] The dissolution was not accepted, although swelling was accepted when it was immersed in toluene and this laminate was left for 24 hours. Moreover, when fire retardancy was evaluated like the example 2, in UL-94 specification, it was a rejection.

[0044] When the example 4 hydrogenation ring breakage norbornene system resin (ZEONEX 280) 20 weight section, the JIKUMIRU peroxide 1 weight section, and the trimethylolpropanetrimesic acid 1 weight section were distributed in the toluene 80 weight section, precipitation etc. was not produced but it became a uniform solution.

[0045] It applied so that it might become 750 micrometers in thickness on the SUS plate which made the mirror plane to the cross-linking norbornene system resin constituent solution

obtained in the example 5 example 4 using the coater. It was left at 120 more degrees C for 10 minutes, and was made to dry for 20 minutes at 60 degrees C. Then, the formed sheet was removed from the SUS plate. The thickness of the obtained sheet was about 150 micrometers.

[0046] The laminating of these eight sheets was carried out, the laminating of the 35-micrometer copper foil was further carried out to both sides, it pressed for 20 minutes, and thermal melting arrival was carried out and the laminate was obtained so that the press temperature of 180 degrees C and press \*\* 40 kgf/cm<sup>2</sup> might make 1mm in thickness.

[0047] Even if this laminate contacted the 260-degree C pewter for 30 seconds, the above, such as exfoliation of copper foil and blistering, was not accepted, but water absorption was [ the dielectric constant in 2x1016 ohms and 1MHz and the dielectric dissipation factor of insulation resistance ] 2.6 and 0.0007 0.02%, respectively.

[0048] The dissolution was not accepted, although swelling was accepted when it was immersed in toluene and this laminate was left for 24 hours. Moreover, when fire retardancy was evaluated like the example 2, in UL-94 specification, it was a rejection.

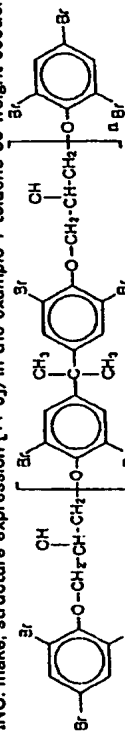
[0049] In the cross-linking norbornene system resin constituent solution obtained in the example 6 example 5, it was immersed and the glass KURORU base material with a thickness of 0.1mm was taken out. After drying the glass-fabrics base material to which impregnation of the cross-linking norbornene system resin constituent was carried out at 60 degrees C for 20 minutes, it was left for 10 minutes at 150 degrees C, and eight prepreps were obtained. 40% of the weight of this prepreg was the cross-linking mold goods of this invention, and thickness was about 110 micrometers.

[0050] The laminating of these eight prepreps was carried out, the laminating of the 35-micrometer copper foil was further carried out to both sides, it pressed for 20 minutes, and thermal melting arrival was carried out and the laminate was obtained so that the press temperature of 180 degrees C and press \*\* 40 kgf/cm<sup>2</sup> might make 1mm in thickness.

[0051] Even if this laminate contacted the 260-degree C pewter for 30 seconds, the above, such as exfoliation of copper foil and blistering, was not accepted, but water absorption was [ the dielectric constant in 1x1017 ohms and 1MHz and the dielectric dissipation factor of insulation resistance ] 2.8 and 0.0011 0.03%, respectively.

[0052] The dissolution was not accepted, although swelling was accepted when it was immersed in toluene and this laminate was left for 24 hours. Moreover, when fire retardancy was evaluated like the example 2, in UL-94 specification, it was a rejection.

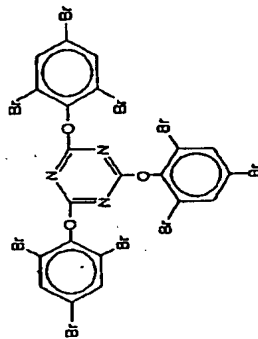
[0053] It is a bromination bisphenol system flame retarder (PURASEFUT EB-242, the MANAC, INC. make, structure expression [\*\* 5]) in the example 7 toluene 80 weight section.



20 weight sections dissolution was carried out. When it mixed with the resin solution 100 weight section which obtained this solution 100 weight section in the example 1, precipitation, separation, etc. were not produced but it became a uniform solution.

[0054] The laminate was obtained by the same approach as an example 3 using the cross-linking norbornene system resin constituent solution obtained in the example 8 example 7. Even if this laminate contacted the 260-degree C pewter for 30 seconds, the above, such as exfoliation of copper foil and blistering, was not accepted, but water absorption was [ the dielectric constant in 5x1016 ohms and 1MHz and the dielectric dissipation factor of insulation resistance ] 3.0 and 0.001 0.02%, respectively. The dissolution was not accepted, even if it was immersed in toluene and left this laminate for 24 hours. Moreover, when fire retardancy was evaluated, in UL-94 specification, it was V-0.

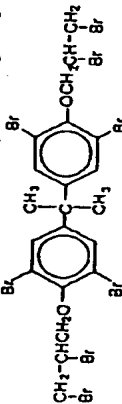
[0055] It is a bromination aromatic series triazine system flame retarder (the Dai-ichi Kogyo Seiyaku Co., Ltd. make, PIROGADO SR 245, structure expression [\*\* 6]) in the example 9 toluene 80 weight section.



20 weight sections dissolution was carried out. When it mixed with the resin solution 100 weight section which obtained this solution 100 weight section in the example 1, precipitation, separation, etc. were not produced but it became a uniform solution.

[0056] The laminate was obtained by the same approach as an example 3 using the cross-linking norbornene system resin constituent solution obtained in the example 10 example 9. Even if this laminate contacted the 260-degree C pewter for 30 seconds, the above, such as exfoliation of copper foil and blistering, was not accepted, but water absorption was [ the dielectric constant in 3x1016 ohms and 1MHz and the dielectric dissipation factor of insulation resistance ] 3.0 and 0.001 0.02%, respectively. The dissolution was not accepted, even if it was immersed in toluene and left this laminate for 24 hours. Moreover, when fire retardancy was evaluated, in UL-94 specification, it was V-0.

[0057] It is a bisphenol system flame retarder (Tejin fire guard 3100, formation incorporated company make, a structure expression [\*\* 7]) in the example 11 toluene 80 weight section.



20 weight sections dissolution was carried out. When it mixed with the resin solution 100 weight section which obtained this solution 100 weight section in the example 1, precipitation, separation, etc. were not produced but it became a uniform solution.

[0058] The laminate was obtained by the same approach as an example 3 using the cross-linking norbornene system resin constituent solution obtained in the example 12 example 11. Even if this laminate contacted the 260-degree C pewter for 30 seconds, the above, such as exfoliation of copper foil and blistering, was not accepted, but water absorption was [ the dielectric constant in 3x1016 ohms and 1MHz and the dielectric dissipation factor of insulation resistance ] 3.0 and 0.001 0.02%, respectively. The dissolution was not accepted, even if it was immersed in toluene and left this laminate for 24 hours. Moreover, when fire retardancy was evaluated, in UL-94 specification, it was V-2.

[0059] The liquefied epoxy system thermosetting constituent (what added the benzyl dimethylamine 0.2 weight section as curing agent in the Epicoat 5046 100 weight section by oil-ized shell compound as hardening mold epoxy compound as diacyanamide 4 weight section, dimethylformamide 14 weight section, and hardening assistant) 70 weight section of example of comparison 1 hyperviscosity was distributed and dissolved into the methyl-ethyl-ketone 100 weight section.

[0060] The glass-fabrics base material with a thickness of 0.1mm was immersed in this solution. After drying the glass-fabrics base material to which impregnation of this epoxy system thermosetting constituent was carried out at 60 degrees C for 10 minutes, it was left for 10 minutes at 150 degrees C, and eight prepreps were obtained. About 50% of the weight of this prepreg was a cross-linking norbornene system resin constituent, and thickness was about 130 micrometers.

[0061] The laminating of this prepreg of eight sheets was carried out, the laminating of the 35-

micrometer copper foil was further carried out to both sides, it pressed for about 90 minutes, and thermal melting arrival was carried out and the laminate was obtained so that the press temperature of 180 degrees C and press pressure 40 kgf/cm2 might make 1mm in thickness. [0062] Although abnormalities, such as exfoliation of copper foil and blistering, were not accepted even if this laminate contacted the 260-degree C pewter for 30 seconds, 0.15%, water absorption was 4.8 and 0.022 and the insulation resistance of absorptivity, a dielectric constant, and a dielectric dissipation factor was not respectively, desirable [ water absorption / the dielectric constant in 1x1015 ohms and 1MHz and the dielectric dissipation factor ] as an electrical insulation material.

[0063] When the example of comparison 2 hydrogenation ring breakage norbornene system resin (ZEONEX 280) 20 weight section and the dicumyl peroxide 1 weight section were distributed in the toluene 80 weight section, precipitation etc. was not produced but it became a uniform solution.

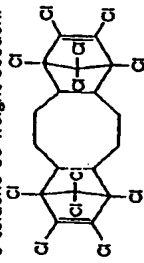
[0064] It applied so that it might become 750 micrometers in thickness on the SUS plate which made the mirror plane to this cross-linking norbornene system resin constituent solution using the coater. Leave it at 120 more degrees C for 10 minutes for 20 minutes, and it was made to dry at 60 degrees C, and removed from the SUS plate after that. The thickness of the obtained sheet was about 150 micrometers.

[0065] The laminating of these eight sheets was carried out, the laminating of the 35-micrometer copper foil was further carried out to both sides, it pressed for 20 minutes, and thermal melting arrival was carried out and the laminate was obtained so that the press temperature of 180 degrees C and press \*\* 40 kgf/cm2 might make 1mm in thickness.

[0066] When this laminate contacted the 260-degree C pewter for 30 seconds, exfoliation of copper foil and generating of blistering were accepted and deformation was accepted further.

[0067] When it was immersed in toluene and this laminate was left for 24 hours, most laminates dissolved.

[0068] It is an annular chloroparaffin system flame retarder (a DEKURO lamp lath, oxy-dental chemical incorporated company make, structure expression [\*\* 8]) to the example of comparison 3 toluene 80 weight section.



20 weight sections were dissolved. When it mixed with the resin solution 100 weight section which obtained this solution 100 weight section in the example 1, it did not dissolve, but precipitation was produced when it was left for one week.

[0069]

[Effect of the Invention] Even if it contacts a 260-degree C pewter for 30 seconds, neither exfoliation of copper foil nor generating of blistering takes place, but it is [ the mold goods which constructed the bridge in the cross-linking norbornene system resin constituent of this invention are excellent in thermal resistance, chemical resistance, moisture resistance, the water resisting property, and the electrical property, and / be / it / hard coming to dissolve in toluene ] excellent [ mold goods ] in especially thermal resistance and chemical resistance, and they do not have nonuniformity, and are useful as the RF circuit board etc.

[Translation done.]

# CROSSLINKABLE NORBORNENE RESIN COMPOSITION AND MOLDING MADE THEREFROM

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C08L65/00; H05K1/03; (IPC1-7): C08L65/00; C08J5/18;  
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## Abstract of JP6248164

**PURPOSE:** To obtain the subject composition which can give a molding improved in electrical insulation properties, heat resistance, chemical resistance, etc., by mixing a thermoplastic hydrogenated ring-opening norbornene resin with an organic peroxide, a crosslinking aid and a specified flame retardant. **CONSTITUTION:** 100 pts.wt. thermoplastic hydrogenated ring-opening norbornene resin of a molecular weight of 10000-200000 and a degree of hydrogenation of 90% or above is melt-mixed with 0.001-30 pts.wt. organic peroxide, 0.1-10 pts.wt. wt., per pt.wt. organic peroxide, crosslinking aid and optionally 5-150 pts.wt. flame retardant of formula I or II (wherein (n) and m1 to M6 integers;  $n \geq 0$ ;  $1 \leq m1 \leq 5$ ;  $1 \leq m25$ ;  $1 \leq m3 \leq 4$ ;  $1 \leq m4 \leq 5$ ;  $1 \leq m5 \leq 5$ ; and  $1 \leq m6 \leq 5$ ) to obtain a resin composition. This resin composition is molded and crosslinked at 80-350 deg.C for 5-120 min to obtain a crosslinked molding having a water absorptivity of 0.03% or below, an insulation resistance of  $10^{15}$  to  $10^{17}$  OMEGA, a dielectric constant of 2.0-2.5 at 1MHz and a dielectric loss tangent of 0.0001-0.0007.

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(33)優先権主張国	日本 (J P)		

(54)【発明の名称】 架橋性ノルボルネン系樹脂組成物、及びそれから成る成形品

## (57)【要約】

【構成】 熱可塑性水素化開環ノルボルネン系樹脂（好ましくは水素添加率90%以上）100重量部に対して有機過酸化物0.001～30重量部、及び架橋助剤（好ましくはアリル系架橋所剤またはメタクリレート系架橋助剤）を有機過酸化物1重量部に対して0.1～10重量部、好ましくは特定構造を有する難燃剤を樹脂100重量部に対して5～150重量部添加し、均一に分散させた架橋性ノルボルネン系樹脂組成物を得、フィルムやブリブregに成形し積層して、加熱圧縮成形して架橋・熱融着させて架橋成形品を得る。

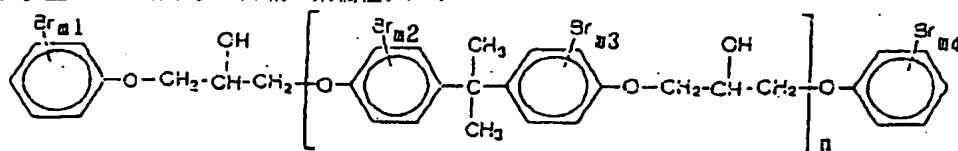
【効果】 耐熱性、耐薬品性、耐湿性、耐水性、電気特性に優れ、ムラのない架橋成形品が得られる。

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## 【特許請求の範囲】

【請求項1】 熱可塑性水素化開環ノルボルネン系樹脂100重量部に対して有機過酸化物0.001~30重量部及び有機過酸化物1重量部に対して架橋助剤0.1~10重量部を分散して成る均一な架橋性ノルボルネン系樹脂組成物。

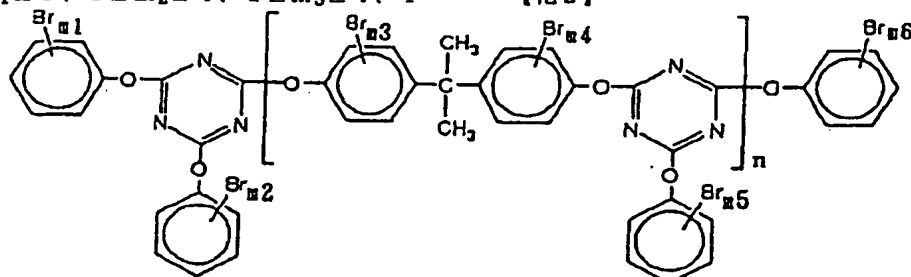
【請求項2】 該水素化開環ノルボルネン系樹脂の水素添加率が90%以上である請求項1記載の架橋性ノルボ



(一般式1中、 $n, m_1, m_2, m_3, m_4$ は整数であり、 $n \geq 0, 1 \leq m_1 \leq 5, 1 \leq m_2 \leq 4, 1 \leq m_3 \leq 4, 1$

$\leq m_4 \leq 5$ である)、または一般式2

## 【化2】



(一般式2中、 $n, m_1, m_2, m_3, m_4, m_5, m_6$ は整数であり、 $n \geq 0, 1 \leq m_1 \leq 5, 1 \leq m_2 \leq 5, 1 \leq m_3 \leq 4, 1 \leq m_4 \leq 4, 1 \leq m_5 \leq 5, 1 \leq m_6 \leq 5$ である)で表される難燃剤を5~150重量部添加して成る請求項1、2、または3記載の架橋性ノルボルネン系樹脂組成物。

【請求項5】 請求項1、2、3、または4記載の架橋性ノルボルネン系樹脂組成物から成る架橋性成形品。

【請求項6】 フィルム、またはシートである請求項5記載の架橋性成形品。

【請求項7】 プリブレグである請求項5記載の架橋性成形品。

【請求項8】 請求項5、6、または7記載の架橋性成形品を加熱し架橋させたものである架橋成形品。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】 本発明は、電気絶縁性に優れた架橋性ノルボルネン系樹脂組成物、それから成る架橋性成形品、及び架橋成形品に関する。

## 【0002】

【従来の技術】 電子計算機、通信機などの精密機器等の回路は、技術の進歩に伴い、演算処理の高速化や高信頼化、高密度化などの要求が高まり、回路基板の多層化、高精度化、微細化など、高性能化が進んでいる。

【0003】 従来、このような回路基板としては、フェノール樹脂、エポキシ樹脂、ポリイミド樹脂、フッ素樹

ルネン系樹脂組成物。

【請求項3】 該架橋助剤がアリル系架橋助剤またはメタクリレート系架橋助剤である請求項1、または2記載の架橋性ノルボルネン系樹脂組成物。

【請求項4】 熱可塑性水素化開環ノルボルネン系樹脂100重量部に一般式1

## 【化1】

脂、あるいはポリブタジエン樹脂などが用いられており、技術の進歩に応じて改良されつつある(特開昭60-84317号、特開昭60-258233号、特開昭60-202130号、特開平3-37256号、特開平3-55237号、特開平3-166256号、特開平3-275760号等)。

【0004】 しかし、フェノール樹脂、エポキシ樹脂、ポリイミド樹脂などの熱硬化性樹脂は、通常、誘電率が4.0以上、誘電正接が0.01以上と高いため電気特性に難があり、これらの樹脂を回路基板等に用いた場合、演算処理の高速化や高信頼化が困難であった。一方、フッ素樹脂、ポリブタジエン樹脂等の熱可塑性樹脂を用いたプリブレグの積層板は、耐熱性に劣るため、ハンダづけの際などに、クラックや剥離が生じることがあり、寸法安定性も悪く、多層化が困難であった。

【0005】 最近、熱可塑性ノルボルネン系樹脂を、有機過酸化物架橋させることにより、耐熱性、耐溶剤性を改良する方法が提案されている。例えば、特開昭62-34924号公報で開示された方法では、樹脂と架橋助剤を混練した後粉碎し、それに有機過酸化物溶液を含浸させ、溶媒を除去した後、プレス成形して架橋する方法が開示されている。しかし、このような手順では、工程が複雑であり、効率が悪い上、有機過酸化物が必ずしも均一に分散しないという問題がある。また、該公報で開示されている熱可塑性ノルボルネン系樹脂はノルボルネン系単量体とエチレンの共重合体であり、開示されてい

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ない水素化開環ノルボルネン系樹脂をこの方法で有機過氧化物で架橋しようとする、しばしば、重合体の分解による分子量の低下が生じ、ハンダづけ等に必要な耐熱性が得られないことが判明した。

【0006】また、特開平2-255848号公報には、水素化開環ノルボルネン系樹脂を含めた熱可塑性ノルボルネン系樹脂に非晶性または低結晶性の $\alpha$ -オレフィン系共重合体及び非晶性または低結晶性のスチレン系共重合体を配合した樹脂組成物を有機過氧化物を用いて架橋することが開示されているが、水素化開環ノルボルネン系樹脂については具体的に架橋された例はなく、これらの特殊な樹脂を配合しない水素化開環ノルボルネン系樹脂を有機過氧化物を用いて架橋することは開示されていない。さらに、該公報では、このような樹脂組成物に有機過氧化物、架橋助剤、難燃剤を配合して架橋する方法と樹脂と有機過氧化物を配合して架橋した後で難燃剤を配合する方法が開示されているが、架橋後に難燃剤を配合する方法では、プリプレグの積層板等に用いる場合に難燃剤が均一に分散しにくく、実用的でないという問題があり、また、架橋前に難燃剤を配合する場合に、樹脂として水素化開環ノルボルネン系樹脂のみを用いた場合は、該公報に例示されている難燃剤では、有機過氧化物で変性してしまい十分な難燃性が得られない、均一に分散しないものがあるという問題があった。

【0007】

【発明が解決しようとする課題】そこで、本発明者らは、耐熱性に優れ、誘電率、誘電正接の低い樹脂から成る成形品の開発を目的に鋭意研究の結果、熱可塑性水素化開環ノルボルネン系樹脂に有機過氧化物及び架橋所剤を均一に分散させると、重合帯の分解を生じることなく、架橋し得ることを見出し、本発明を完成させるに至った。

【0008】

【課題を解決するための手段】かくして、本発明によれば、熱可塑性水素化開環ノルボルネン系樹脂100重量部に対して有機過氧化物0.001~30重量部及び有機過氧化物1重量部に対して架橋助剤0.1~10重量部を分散して成る均一な架橋性ノルボルネン系樹脂組成物、該架橋性ノルボルネン系樹脂組成物から成る架橋性成形品、及び該架橋性成形品を加熱し架橋させたものである架橋成形品が提供される。

【0009】（熱可塑性水素化開環ノルボルネン系樹脂）本発明に用いられる熱可塑性水素化開環ノルボルネン系樹脂は、特開平3-14882号や特開平3-122137号等で公知の樹脂であり、具体的には、ノルボルネン系単量体の開環重合体の水素添加物である。

【0010】ノルボルネン系単量体も、上記公報や特開平2-227424号、特開平2-276842号などで公知の単量体であって、例えば、ノルボルネン、そのアルキル、アルキリデン、芳香族置換誘導体およびこれ

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ら置換または非置換のオレフィンのハロゲン、水酸基、エステル基、アルコキシ基、シアノ基、アミド基、イミド基、シリル基等の極性基置換体、例えば、2-ノルボルネン、5-メチル-2-ノルボルネン、5,5-ジメチル-2-ノルボルネン、5-エチル-2-ノルボルネン、5-ブチル-2-ノルボルネン、5-エチリデン-2-ノルボルネン、5-メトキシカルボニル-2-ノルボルネン、5-シアノ-2-ノルボルネン、5-メチル-5-メトキシカルボニル-2-ノルボルネン、5-フェニル-2-ノルボルネン、5-フェニル-5-メチル-2-ノルボルネン、5-ヘキシル-2-ノルボルネン、5-オクチル-2-ノルボルネン、5-オクタデシル-2-ノルボルネン等；ノルボルネンに一つ以上のシクロペンタジエンが付加した単量体、その上記と同様の誘導体や置換体、例えば、1,4:5,8-ジメタノ-1,2,3,4,4a,5,8,8a-2,3-シクロペンタジエノナフタレン、6-メチル-1,4:5,8-ジメタノ-1,4,4a,5,6,7,8,8a-オクタヒドロナフタレン、1,4:5,10:6,9-トリメタノ-1,2,3,4,4a,5,5a,6,9,9a,10,10a-ドデカヒドロ-2,3-シクロペンタジエノアントラセン等；シクロペンタジエンの多量体である多環構造の単量体、その上記と同様の誘導体や置換体、例えば、ジシクロペンタジエン、2,3-ジヒドロジシクロペンタジエン等；シクロペンタジエンとテトラヒドリンデン等との付加物、その上記と同様の誘導体や置換体、例えば、1,4-メタノ-1,4,4a,4b,5,8,8a,9a-オクタヒドロフルオレン、5,8-メタノ-1,2,3,4,4a,5,8,8a-オクタヒドロ-2,3-シクロペンタジエノナフタレン等；等が挙げられる。

【0011】ノルボルネン系単量体の開環重合は公知の方法でよく、必要に応じて、他の共重合可能な単量体と共重合してもよい。重合体を特開平3-95235号等で公知の方法により、 $\alpha$ 、 $\beta$ -不飽和カルボン酸及び/またはその誘導体、スチレン系炭化水素、オレフィン系不飽和結合及び加水分解可能な基を持つ有機ケイ素化合物、不飽和エポキシ単量体を用いて変性させてもよい。これらの樹脂を水素添加することにより熱可塑性水素化開環ノルボルネン系樹脂とする。水素化後に樹脂を変性してもよい。

【0012】水素化開環ノルボルネン系樹脂の分子量はシクロヘキサンを溶媒とするGPC（ゲル・パージェーション・クロマトグラフィ）法で測定したポリスチレン換算値で、10,000~200,000、好ましくは20,000~100,000、より好ましくは25,000~50,000である。数平均分子量が小さすぎると機械的強度が劣り、大きすぎると成形性が悪くなる。また、水素添加率は耐熱劣化性や耐光劣化性を向上させるために、90%以上、好ましくは95%以上、よ



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り好ましくは、99%以上である。

【0013】本発明で用いる水素化開環ノルボルネン系樹脂には、均一に分散できる限りにおいて、所望により、フェノール系やリン系等の老化防止剤；フェノール系等の熱劣化防止剤；ベンゾフェノン系等の紫外線安定剤；アミン系等の帯電防止剤；脂肪族アルコールのエステル、多価アルコールの部分エステル及び部分エーテル等の滑剤；等の各種添加剤を添加してもよい。

【0014】（有機過酸化物）本発明に用いる有機過酸化物は、特に限定されず、特開昭62-34924号公報等で公知のものでよく、例えば、*t*-ブチルヒドロパーオキシド、*p*-メンタンヒドロパーオキシド、クメンヒドロパーオキシド等のヒドロパーオキシド類；ジクミンパーオキシド、*t*-ブチルクミンパーオキシド、 $\alpha$ 、 $\alpha'$ -ビス（*t*-ブチルパーオキシ-*m*-イソプロピル）ベンゼン等のジアルキルパーオキシド類；ジプロピオニルパーオキシド、ベンゾイルパーオキシド等のジアシルパーオキシド類；2,5-ジメチル-2,5-ジ（*t*-ブチルパーオキシ）ヘキサン、2,5-ジメチル-2,5-ジ（*t*-ブチルパーオキシ）ヘキシン-3,1,3-ジ（*t*-ブチルパーオキシイソプロピル）ベンゼン等のパーオキシケタール類；*t*-ブチルパーオキシアセテート、*t*-ブチルパーオキシベンゾエート等のパーオキシエステル類；*t*-ブチルパーオキシイソプロピルカルボナート、ジ（イソプロピルパーオキシ）ジカルボナート等のパーオキシカルボナート等のケトンパーオキシド類；等が挙げられる。

【0015】（架橋助剤）本発明に用いる架橋助剤も、特に限定されず、特開昭62-34924号公報等で公知のものでよく、キノンジオキシム、ベンゾキノンジオキシム、*p*-ニトロソフェノール等のオキシム・ニトロソ系架橋助剤；N,N-*m*-フェニレンビスマレイミド等のマレイミド系架橋助剤；ジアリルフタレート、トリアリルシアヌレート、トリアリルイソシアヌレート等のアリル系架橋助剤；エチレングリコールジメタクリレート、トリメチロールプロパントリメタクリレート

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等のメタクリレート系架橋助剤；ビニルトルエン、エチルビニルベンゼン、ジビニルベンゼン等のビニル系架橋助剤；等が例示される。中でも、アリル系架橋助剤、メタクリレート系架橋助剤が、均一に分散させやすく、好ましい。

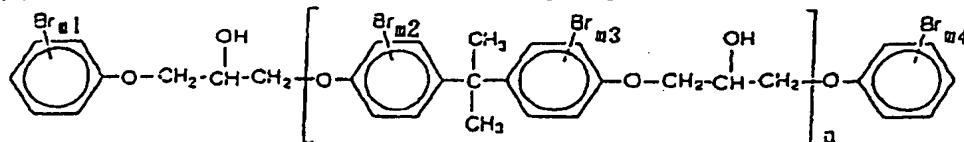
【0016】（架橋性ノルボルネン系樹脂組成物）本発明の架橋性ノルボルネン系樹脂組成物は、熱可塑性水素化開環ノルボルネン系樹脂に有機過酸化物と架橋助剤を添加して成る均一な組成物である。

【0017】有機過酸化物の添加量が少なすぎると架橋が起こり難くなることから、熱可塑性水素化開環ノルボルネン系樹脂100重量部に対して0.001重量部以上、好ましくは0.01重量部以上、より好ましくは0.05重量部以上、特に好ましくは1重量部以上の有機過酸化物を添加する。また、有機過酸化物の添加量が多すぎると架橋した樹脂の電気特性、耐水性、耐湿性等が低下するため、熱可塑性水素化開環ノルボルネン系樹脂100重量部に対して30重量部、好ましくは15重量部、より好ましくは10重量部、特に好ましくは5重量部を超えないように有機過酸化物を添加する。

【0018】また、架橋助剤の添加量は、有機過酸化物1重量部に対して0.1~10重量部、好ましくは0.2~5重量部である。架橋助剤の添加量が少なすぎると架橋が起こりにくく、水素化開環ノルボルネン系樹脂が分解して分子量が低下するため、ハンダづけに必要な耐熱性が得られない。架橋助剤の添加量が多すぎると架橋した樹脂の電気特性、耐水性、耐湿性等が低下するため好ましくない。

【0019】さらに、本発明の架橋成形品の難燃性を高めるためには、本発明のノルボルネン系樹脂組成物には、難燃剤を均一に分散させることが好ましい。本発明において用いる難燃剤は、樹脂組成物として均一に分散させることができるものであり、また、樹脂組成物として配合した状態や、架橋反応の工程において、有機過酸化物によって分解、変性、変質しないものが好ましい。具体的には一般式1

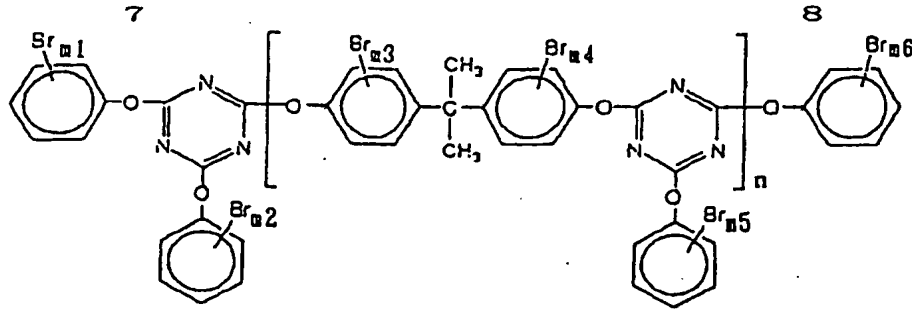
【化3】



（一般式1中、 $n$ 、 $m_1$ 、 $m_2$ 、 $m_3$ 、 $m_4$ は整数であり、 $n \geq 0$ 、 $1 \leq m_1 \leq 5$ 、 $1 \leq m_2 \leq 4$ 、 $1 \leq m_3 \leq 4$ 、 $1 \leq m_4 \leq 5$ 、好ましくは $2 \leq m_1 \leq 4$ 、 $2 \leq m_2 \leq 3$ 、

$\leq m_3 \leq 3$ 、 $2 \leq m_4 \leq 4$ 、特に好ましくは $m_1 = 3$ 、 $m_2 = 2$ 、 $m_3 = 2$ 、 $m_4 = 3$ である）または一般式2

【化4】



(一般式2中、 $n$ 、 $m_1$ 、 $m_2$ 、 $m_3$ 、 $m_4$ 、 $m_5$ 、 $m_6$ は整数であり、 $n \geq 0$ 、 $1 \leq m_1 \leq 5$ 、 $1 \leq m_2 \leq 5$ 、 $1 \leq m_3 \leq 4$ 、 $1 \leq m_4 \leq 4$ 、 $1 \leq m_5 \leq 5$ 、 $1 \leq m_6 \leq 5$ 、好ましくは $2 \leq m_1 \leq 4$ 、 $2 \leq m_2 \leq 4$ 、 $2 \leq m_3 \leq 3$ 、 $2 \leq m_4 \leq 3$ 、 $2 \leq m_5 \leq 4$ 、 $2 \leq m_6 \leq 4$ 、特に好ましくは $m_1 = 3$ 、 $m_2 = 3$ 、 $m_3 = 2$ 、 $m_4 = 2$ 、 $m_5 = 3$ 、 $m_6 = 3$ である)で表される難燃剤が均一に分散でき、かつ有機過酸化物によって分解、変性、変質しない。添加量は水素化開環ノルボルネン系樹脂100重量部に対して5~150重量部、好ましくは20~140重量部、特に好ましくは40~120重量部である。

【0020】水素化開環ノルボルネン系樹脂に有機過酸化物と架橋助剤、また必要に応じて難燃剤を均一に分散する方法は、特に限定されず、例えば、開環樹脂溶液中で混合・分散させて溶媒を除去する方法、開環樹脂が溶融した状態で混合・分散させる方法等がある。開環樹脂の溶媒も開環樹脂を溶解するものであれば特に限定されず、例えば、トルエン、キシレン、エチルベンゼン、クロロベンゼン等を用いることができる。なお、開環樹脂を溶融させて有機過酸化物等を混合・分散する方法においては、架橋しない温度で、溶融・混合・分散ができなければならず、開環樹脂、有機過酸化物、架橋助剤の組み合わせによっては、この方法は使用できない。開環樹脂溶液中で混合・分散させる方法においても、溶媒を除去するために加熱する場合、架橋が起こらないように温度設定をする必要がある。

【0021】(架橋性成形品) 本発明においては、架橋性ノルボルネン系樹脂組成物を成形した後、架橋させて架橋性成形品を得る。

【0022】架橋性ノルボルネン系樹脂組成物を成形する方法は、成形途中での架橋により成形性の悪化が起こらないように、溶媒に溶解して成形するか、架橋しない温度、または架橋速度が十分に遅い温度で溶融して成形する。溶媒としては、前述の水素化開環ノルボルネン系樹脂を溶解する溶剤を用いる。一般的には、溶媒に溶解して成形する。

【0023】具体的には、溶媒に溶解した架橋性ノルボルネン系樹脂組成物を流延して溶媒を除去してシートやフィルムに成形するか、ガラスクロス、アラミドクロス、ポリエステルクロス、ナイロンクロス等のクロス状基材、これらと同じ材質のマット状基材、不織布、クラ

フト紙、リントー紙等の基材に含浸させて成形する。基材に樹脂組成物を含浸させた架橋性成形品としては、プリプレグが例示される。

【0024】(架橋) 本発明においては、架橋性成形品を単独で、または積層して、一定温度以上に加熱して架橋させて架橋成形品を得る。架橋反応を生じさせる温度は、主として有機過酸化物と架橋助剤の組み合わせによって決められるが、一般には、80~350℃、好ましくは120℃~300℃、さらに好ましくは150~250℃の温度に加熱することにより架橋する。また、架橋時間は、有機過酸化物の半減期の4倍程度にするのが好ましく、一般には、5~120分、好ましくは10~90分、さらに好ましくは20~60分である。架橋性成形品を積層して架橋する場合、各層の間で熱融着・架橋が起こり、一体の架橋成形品が得られる。

【0025】(架橋成形品) 本発明の架橋成形品として、架橋させたものとして、積層板、回路基板、層間絶縁膜、防湿層成形用フィルム等が例示される。

【0026】本発明の架橋成形品は、通常、吸水率が0.03%以下、絶縁抵抗が $10^{15} \sim 10^{17} \Omega$ 、1MHzでの誘電率、誘電正接がそれぞれ2.0~2.5、0.0001~0.0007であり、従来の熱硬化性樹脂製成形品に比べて、耐水性、電気特性が優れている。一方、耐熱性は従来の熱硬化性樹脂製成形品と同等であり、銅箔を積層した積層板に260℃のハンダを30秒接触させても、銅箔の剥離やフクレの発生等の以上は認められない。これらのことから、本発明の架橋成形品である積層板は回路基板としても好ましいものである。

【0027】また、本発明の架橋成形品は、難燃性に優れたもの、具体的には、UL-94規格においてV-2またはそれよりも優れた難燃性を示すものが好ましく、V-1またはV-0の難燃性を示すものがより好ましく、V-0の難燃性を示すものが特に好ましい。そのような架橋性成形品を得るためには、前述のような難燃剤を含有している架橋性ノルボルネン系樹脂組成物を用いなければならない。

【0028】(プリプレグ) 本発明の架橋性成形品の具体例の一つであるプリプレグにおいては、その基材は特に限定されず、一般にプリプレグと基板として用いられるガラスクロス、アラミドクロス、ポリエステルクロス、ナイロンクロス等のクロス状基材、これらと同じ材

質のマット状基材、不織布、クラフト紙、リントー紙等を用いることができる。

【0029】本発明の架橋性ノルボルネン系樹脂組成物を用いたプリブレグの製造は、常法に従えばよく、例えば、トルエン、シクロヘキサン、キシレン等の溶剤中に架橋性ノルボルネン系樹脂組成物を濃度5～50重量%程度に溶解させ、その溶液中に基材を含浸させた後、乾燥させて、溶剤を除去すればよい。一般にプリブレグは50～500 $\mu$ m程度の厚さになるようにすることが好ましい。

【0030】(シート) 本発明の架橋性成形品の具体例の一つであるシートを製造する方法は、特に限定されない。一般にはキャスト法が用いられる。例えば、トルエン、キシレン、シクロヘキサン等の溶剤中に本発明の架橋性ノルボルネン系樹脂組成物を濃度5～50重量%程度になるように溶解、分散させ、平滑面上に流延または塗布し、乾燥等により溶剤を除去し、平滑面から剝離してシートを得る。乾燥により溶剤を除去する場合は、急速な乾燥により発泡することのない方法を選択することが好ましく、例えば、低温である程度溶剤を揮発させた後、温度を上げて溶剤を十分に揮発させるようにすればよい。平滑面としては、鏡面処理した金属板や樹脂製のキャリアフィルム等を用いればよい。樹脂製のキャリアフィルムを用いる場合、キャリアフィルムの素材の耐溶剤性、耐熱性に注意して、用いる溶剤や乾燥条件を決めなければならない。キャスト法により得られるシートは、一般に10 $\mu$ m～1mm程度の厚みを有する。これらのシートは、架橋することにより、層間絶縁膜、防湿層形質用フィルム等として用いることができる。また、次に記載する積層板の製造に用いることもできる。

【0031】(積層板) 本発明の架橋成形品の具体例の一つである積層板は、前述のプリブレグ、及び/または未架橋のシートを積み重ね、加熱圧縮成形して架橋・熱融着させることにより、必要な厚さにしたものである。積層板を回路基板として用いる場合には、例えば、金属箔等からなる配線用導電層を積層したり、表面のエッチング処理等により回路を形成する。配線用導電層は完成品である積層板の外部表面に積層するのみでなく、目的等によっては、積層板の内部に積層されていてもよい。エッチング処理等の二次加工時の反り防止のためには、上下対象に組み合わせて積層することが好ましい。例えば、重ねたプリブレグ及び/またはシートの表面を、用いた架橋性ノルボルネン系樹脂に応じた熱融着する温度以上、通常150～300℃程度に加熱し、30～80kgf/cm<sup>2</sup>程度に加圧して、各層の間に架橋・熱融着させて積層板を得る。

【0032】

【実施例】以下に実施例、比較例をあげて、本発明をさらに具体的に説明する。なお、絶縁抵抗、誘電率、誘電

正接、吸水率はJIS C 6481により測定し、可燃性はUL-94規格に従って以下の方法で評価した。

【0033】厚さ1/16インチの試験片を用い、試験片の上端をクランプで止めて試験片を垂直に固定し、試験片の下12インチのところに木綿を敷く。試験片の下端にガスバーナーの火を10秒間当て、試験片の1回目の燃焼時間を測定し、火が消えたら再び下端にガスバーナーの火を10秒間当て、試験片の2回目の燃焼時間を測定する。試験片5個について1回目の燃焼時間と2回目の燃焼時間の10個のデータの総和をTとし、最大のデータをMとするときに、以下の基準により、V-0、V-1、V-2、不合格と判断した。

V-0: Tが50秒以下、Mが10秒以下、クランプまで燃え上がらず、かつ炎のついた溶融物が落下して木綿が着火しない。

V-1: Tが250秒以下、Mが30秒以下、クランプまで燃え上がらず、かつ炎のついた溶融物が落下して木綿が着火しない。

V-2: Tが250秒以下、Mが30秒以下、クランプまで燃え上がらないが、炎のついた溶融物が落下して木綿が着火した。

不合格: 上記のV-0、V-1、V-2の要件を満たさない。

#### 【0034】実施例1

水素化開環ノルボルネン系樹脂(ZEONEX 280、日本ゼオン株式会社製、ガラス転移温度140℃、数平均分子量約28,000、水素添加率99.7%以上)20重量部と $\alpha$ 、 $\alpha'$ -ビス(4-tert-ブチルパーオキシ-1-メチル-2-プロピル)ベンゼン1重量部、ジアリルフタレート1重量部をトルエン80重量部中に分散させたところ、沈澱なども生じず、均一な溶液となった。

#### 【0035】実施例2

実施例1で得た架橋性ノルボルネン系樹脂組成物溶液を塗工機を用いて、鏡面に仕上げたSUS板上に厚さ750 $\mu$ mになるように塗布した。60℃で20分間、さらに120℃で10分放置して乾燥させた。その後、形成されたシートをSUS板から剝した。得られたシートの厚さは約150 $\mu$ mであった。

【0036】このシート8枚を積層し、さらに両面に35 $\mu$ mの銅箔を積層して、プレス温度180℃、プレス圧40kgf/cm<sup>2</sup>で厚さ1mmになるように20分プレスして熱融着させて積層板を得た。

【0037】この積層板は260℃のハンダを30秒接触させても、銅箔の剝離やフクレ等の以上は認められず、吸水率は0.01%以下、絶縁抵抗は4×10<sup>16</sup> $\Omega$ 、1MHzでの誘電率、誘電正接はそれぞれ、2.4、0.0005であった。

【0038】この積層板をトルエンに浸漬して24時間放置したところ、膨潤が認められたが、溶解は認められなかった。

【0039】また、シート13枚を積層して、プレス温度180℃、プレス圧40kgf/cm<sup>2</sup>で厚さ1/16インチになるように20分プレスして熱融着させて難燃性試験用試験片を得た。この試験片を用いて難燃性を評価したところ、UL-94規格において、不合格であった。

#### 【0040】実施例3

実施例1で得た架橋性ノルボルネン系樹脂組成物溶液に厚さ0.1mmのガラスクロス基材を浸漬して、取り出した。架橋性ノルボルネン系樹脂組成物を含浸させたガラスクロス基材を60℃で20分乾燥させた後、150℃で10分間放置して、プリプレグを8枚得た。このプリプレグの40重量%は本発明の架橋性成形品であり、厚さは約110μmであった。

【0041】このプリプレグ8枚を積層し、さらに両面に35μmの銅箔を積層して、プレス温度180℃、プレス圧40kgf/cm<sup>2</sup>で厚さ1mmになるように20分プレスして熱融着させて積層板を得た。

【0042】この積層板は260℃のハンダを30秒接触させても、銅箔の剥離やフクレ等の以上は認められず、吸水率は0.01%、絶縁抵抗は1×10<sup>17</sup>Ω、1MHzでの誘電率、誘電正接はそれぞれ、2.7、0.0009であった。

【0043】この積層板をトルエンに浸漬して24時間放置したところ、膨潤が認められたが、溶解は認められなかった。また、実施例2と同様にして難燃性を評価したところ、UL-94規格において、不合格であった。

#### 【0044】実施例4

水素化開環ノルボルネン系樹脂(ZEONEX 280)20重量部とジクミルパーオキシド1重量部、トリメチロールプロパントリメタクリレート1重量部をトルエン80重量部中に分散させたところ、沈澱なども生じず、均一な溶液となった。

#### 【0045】実施例5

実施例4で得た架橋性ノルボルネン系樹脂組成物溶液を塗工機を用いて、鏡面に仕上げたSUS板上に厚さ750μmになるように塗布した。60℃で20分間、さらに120℃で10分間放置して乾燥させた。その後、形成されたシートをSUS板から剥した。得られたシートの厚さは約150μmであった。

)を20重量部溶解した。この溶液100重量部を実施例1で得た樹脂溶液100重量部と混合したところ、沈澱、分離なども生じず、均一な溶液となった。

#### 【0054】実施例8

【0046】このシート8枚を積層し、さらに両面に35μmの銅箔を積層して、プレス温度180℃、プレス圧40kgf/cm<sup>2</sup>で厚さ1mmになるように20分プレスして熱融着させて積層板を得た。

【0047】この積層板は260℃のハンダを30秒接触させても、銅箔の剥離やフクレ等の以上は認められず、吸水率は0.02%、絶縁抵抗は2×10<sup>16</sup>Ω、1MHzでの誘電率、誘電正接はそれぞれ、2.6、0.0007であった。

【0048】この積層板をトルエンに浸漬して24時間放置したところ、膨潤が認められたが、溶解は認められなかった。また、実施例2と同様にして難燃性を評価したところ、UL-94規格において、不合格であった。

#### 【0049】実施例6

実施例5で得た架橋性ノルボルネン系樹脂組成物溶液に厚さ0.1mmのガラスクロス基材を浸漬して、取り出した。架橋性ノルボルネン系樹脂組成物を含浸させたガラスクロス基材を60℃で20分乾燥させた後、150℃で10分間放置して、プリプレグを8枚得た。このプリプレグの40重量%は本発明の架橋性成形品であり、厚さは約110μmであった。

【0050】このプリプレグ8枚を積層し、さらに両面に35μmの銅箔を積層して、プレス温度180℃、プレス圧40kgf/cm<sup>2</sup>で厚さ1mmになるように20分プレスして熱融着させて積層板を得た。

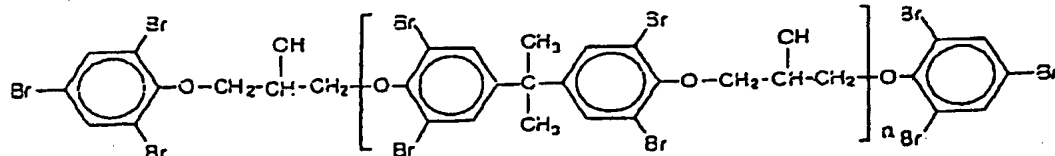
【0051】この積層板は260℃のハンダを30秒接触させても、銅箔の剥離やフクレ等の以上は認められず、吸水率は0.03%、絶縁抵抗は1×10<sup>17</sup>Ω、1MHzでの誘電率、誘電正接はそれぞれ、2.8、0.0011であった。

【0052】この積層板をトルエンに浸漬して24時間放置したところ、膨潤が認められたが、溶解は認められなかった。また、実施例2と同様にして難燃性を評価したところ、UL-94規格において、不合格であった。

#### 【0053】実施例7

トルエン80重量部中に臭素化ビスフェノール系難燃剤(ブラセフティEB-242、マナック株式会社製、構造式

【化5】



実施例7で得た架橋性ノルボルネン系樹脂組成物溶液を用いて、実施例3と同様の方法で積層板を得た。この積層板は、260℃のハンダを30秒接触させても、銅箔の剥離やフクレなどの以上は認められず、吸水率は0.

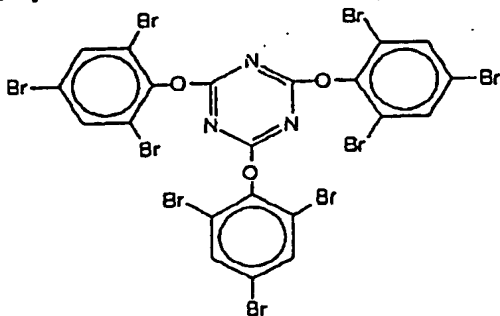
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0.2%、絶縁抵抗は $5 \times 10^{16} \Omega$ 、1MHzでの誘電率、誘電正接はそれぞれ、3.0、0.001であった。この積層板をトルエンに浸漬して24時間放置しても溶解は認められなかった。また、難燃性を評価したところ、UL-94規格において、V-0であった。

#### 【0055】実施例9

トルエン80重量部中に臭素化芳香族トリアジン系難燃剤（第一工業製薬株式会社製、ピロガードSR245、構造式

#### 【化6】



）を20重量部溶解した。この溶液100重量部を実施例1で得た樹脂溶液100重量部と混合したところ、沈殿、分離なども生じず、均一な溶液となった。

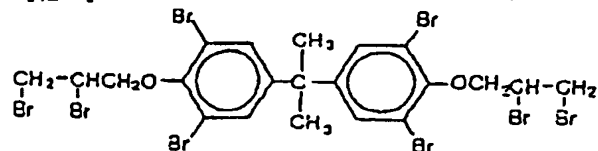
#### 【0056】実施例10

実施例9で得た架橋性ノルボルネン系樹脂組成物溶液を用いて、実施例3と同様の方法で積層板を得た。この積層板は、260℃のハンダを30秒接触させても、銅箔の剥離やフクレなどの以上は認められず、吸水率は0.02%、絶縁抵抗は $3 \times 10^{16} \Omega$ 、1MHzでの誘電率、誘電正接はそれぞれ、3.0、0.001であった。この積層板をトルエンに浸漬して24時間放置しても溶解は認められなかった。また、難燃性を評価したところ、UL-94規格においてV-0であった。

#### 【0057】実施例11

トルエン80重量部中にビスフェノール系難燃剤（ファイヤーガード3100、帝人化成株式会社製、構造式

#### 【化7】



）を20重量部溶解した。この溶液100重量部を実施例1で得た樹脂溶液100重量部と混合したところ、沈殿、分離なども生じず、均一な溶液となった。

#### 【0058】実施例12

実施例11で得た架橋性ノルボルネン系樹脂組成物溶液を用いて、実施例3と同様の方法で積層板を得た。この積層板は、260℃のハンダを30秒接触させても、銅

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箔の剥離やフクレなどの以上は認められず、吸水率は0.02%、絶縁抵抗は $3 \times 10^{16} \Omega$ 、1MHzでの誘電率、誘電正接はそれぞれ、3.0、0.001であった。この積層板をトルエンに浸漬して24時間放置しても溶解は認められなかった。また、難燃性を評価したところ、UL-94規格においてV-2であった。

#### 【0059】比較例1

高粘度の液状のエポキシ系熱硬化性組成物（硬化型エポキシ系化合物として油化シェル社製のエピコート5046 100重量部に、硬化剤としてジシアンジアミド4重量部、ジメチルホルムアミド14重量部、硬化助剤としてベンジルジメチルアミン0.2重量部を添加したもの）70重量部をメチルエチルケトン100重量部中に分散、溶解させた。

【0060】この溶液に厚さ0.1mmのガラスクロス基材を浸漬した。このエポキシ系熱硬化性組成物を含浸させたガラスクロス基材を60℃で10分乾燥させた後、150℃で10分間放置して、プリプレグを8枚得た。このプリプレグの約50重量%は架橋性ノルボルネン系樹脂組成物であり、厚さは約130μmであった。

【0061】この8枚のプリプレグを積層し、さらに両面に35μmの銅箔を積層して、プレス温度180℃、プレス圧力40kgf/cm<sup>2</sup>で、厚さ1mmになるように約90分プレスして熱融着させて積層板を得た。

【0062】この積層板は、260℃のハンダを30秒接触させても、銅箔の剥離やフクレ等の異常は認められなかったが、吸水率は0.15%、絶縁抵抗は $1 \times 10^{15} \Omega$ 、1MHzでの誘電率、誘電正接はそれぞれ、4.8、0.022であり、吸水性、誘電率、誘電正接が電気絶縁材料として好ましいものではなかった。

#### 【0063】比較例2

水素化開環ノルボルネン系樹脂（ZEONEX 280）20重量部とジクミルパーオキサイド1重量部をトルエン80重量部中に分散させたところ、沈殿等生じず、均一な溶液となった。

【0064】この架橋性ノルボルネン系樹脂組成物溶液を、塗工機を用いて、鏡面に仕上げたSUS板上に厚さ750μmになるように塗布した。60℃で20分、さらに120℃で10分放置して乾燥させ、その後SUS板から剥した。得られたシートの厚さは約150μmであった。

【0065】このシート8枚を積層し、さらに両面に35μmの銅箔を積層して、プレス温度180℃、プレス圧40kgf/cm<sup>2</sup>で厚さ1mmになるように20分プレスして熱融着させて積層板を得た。

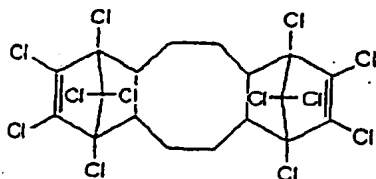
【0066】この積層板は、260℃のハンダを30秒接触させると、銅箔の剥離、フクレの発生が認められ、さらに変形が認められた。

【0067】この積層板をトルエンに浸漬して24時間放置したところ、積層板の大部分が溶解した。

## 【0068】比較例3

トルエン80重量部に環状クロロパラフィン系難燃剤  
(デクロランプラス、オキシデンタルケミカル株式会社  
製、構造式

## 【化8】



20重量部を溶解した。この溶液100重量部を実施  
例1で得た樹脂溶液100重量部と混合したところ、溶  
解せず、一週間放置すると沈澱を生じた。

## 【0069】

【発明の効果】本発明の架橋性ノルボルネン系樹脂組成  
物を架橋した成形品は、耐熱性、耐薬品性、耐湿性、耐  
水性、電気特性に優れており、260℃のハンダを30  
秒接触させても銅箔の剥離やフクレの発生等が起こら  
ず、トルエンに溶解しにくくなるなど、特に耐熱性、耐  
薬品性に優れ、またムラがなく、高周波回路基板等とし  
て有用である。

フロントページの続き

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